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ABSTRACT

ChemSource is designed as a strategy to help preservice and inservice high school chemistry teachers promote student learning more effectively. Its major premise is that well-designed laboratory investigations are an important avenue for cultivating student interest, engagement, and meaningful learning in chemistry. The SourceBook component of ChemSource is a resource containing 36 content modules and additional supporting materials which aim at providing specific teaching tips and the best available instructional ideas and information gleaned from experienced, successful chemistry teachers. Each content module features: Content-in-a-Nutshell; Laboratory Activities; Demonstrations; Common Misconceptions; Humor; Applications and Implications; Analogies; Reference Resources; History; and Media. General materials on pedagogy, classroom management, safety, teaching chemistry to the disabled, and other useful resources and tabulations precede and follow the content modules. Volume 2 includes the following: Chemical Equilibrium; Food and Chemistry; Forensic Chemistry; Gases; Molecular Geometry; Halogens; Industrial Inorganic Chemistry; Instrumentation; Materials Science: Ceramics and Glasses; Chemistry in Medicine; and The Mole. (JRH)

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SourceBook

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VOLUME 2

ChemSource

Instructional Resources for Preservice and Inservice Chemistry Teachers

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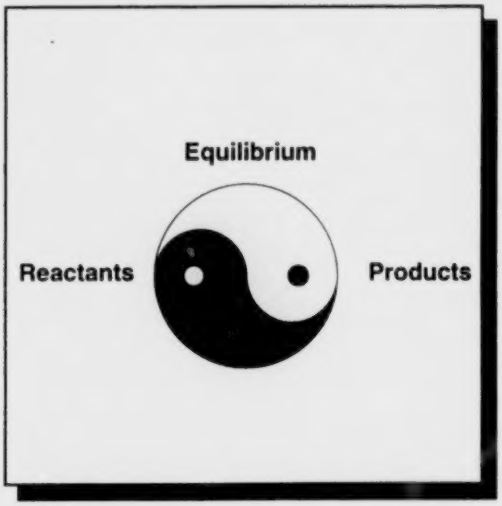

ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

CHEMICAL EQUILIBRIUM

Topic Overview

CONTENT IN A NUTSHELL

Up to this point, chemical reactions have likely been presented to students as being either "complete" or having "no reaction." As a consequence, it is probably not surprising that students are puzzled by chemical reactions where constant amounts of reactants and products are present simultaneously. This phenomenon is because chemical reactions can be reversible. Consider the reaction between nitrogen oxide and ozone represented by the equation:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Using a simple collision theory model of reaction, NO and O_3 molecules can collide, rearrange their atoms, and form NO_2 and O_2 molecules as products. But if this is so, why can't NO_2 and O_2 molecules collide and reform NO and O_3 molecules? The answer is that they can; the reaction is probably better represented by the equation

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

The rate at which NO_2 and O_2 form varies because of the changing concentrations of NO and O_3 as they are used up while being converted to NO_2 and O_2. The same is true for the reverse reaction. Eventually, the rates of the forward and reverse reactions become the same, and the consequence is a state of "balance" or "equilibrium" among the amounts of NO, O_3, NO_2, and O_2 present. Although the reaction appears to have ceased on the macroscopic scale, the forward and reverse reactions continue at the molecular level. This is a "dynamic" equilibrium in contrast to a "static" equilibrium as represented, for example, by a balanced see-saw.

Several examples of dynamic equilibria (as physical changes) may already be familiar to your students. When water evaporates in a closed container, a constant "vapor pressure" is reached. This pressure is exerted by the water vapor molecules when the rate of evaporation is equal to the rate of condensation. Also, in the dissolving of a solid in a liquid solvent, a limit is reached where no more solid will dissolve. This saturation point is reached when the rate of dissolution is equal to the rate of crystallization.

In quantitative terms, chemists are interested in the position of equilibrium, *i.e.*, to what extent the reaction has approached completion when the equilibrium state is reached (*i.e.*, is the reaction 90% complete, 60% complete?). The extent of completion for chemical reactions varies with different reactions. It is usually expressed as the ratio of concentrations of products to reactants (which is theoretically a constant value, K, at a fixed temperature). Specifically, for the hypothetical reaction: $aA + bB \rightleftharpoons cC + dD$, where capital letters represent reactants and products and lowercase letters represent coefficients: $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

PLACE IN THE CURRICULUM

The position of an equilibrium can be shifted toward reactants or products according to LeChatelier's principle (a stress placed on a system at equilibrium will cause a shift that minimizes the stress). Factors (stresses) that influence chemical equilibrium positions are those that affect the rates of forward reactions differently from the rates of reverse reactions. The principal factors are concentration effects and temperature effects. Pressure effects are often included in this list, but the ideal gas law shows that pressure can only be changed by changing concentration (concentration is equal to n/V; consequently any changes in amount of gas or volume of gas will change the concentration), or by changing the temperature.

Equilibrium is usually considered a "later" topic in first-year chemistry. When it is taught, there are three different levels to approaching the content: (1) limiting instruction to descriptive or qualitative issues (LeChatelier's principle), (2) interpreting values of K (*e.g.*, weak *vs.* strong acids), and (3) a complete quantitative approach (calculating values of K). The focus of this module is on the qualitative level of equilibrium, leaving quantitative aspects to *Extensions and Projects*.

CENTRAL CONCEPTS

1. The products of a chemical reaction can often react and reform the reactants (reversibility).
2. A chemical system can reach a state of dynamic balance between its forward and reverse reactions. This state is called chemical equilibrium.
3. A stress placed on a system at equilibrium will cause a shift that minimizes the stress (LeChatelier's Principle).
4. The concentrations of reactants and products in a chemical system at equilibrium are related mathematically (Law of Mass Action; the equilibrium constant).

RELATED CONCEPTS

1. **Gases (Gas Laws)**. The general gas law describes the relationship among the variables P, T, V, n. Relationships often described in textbooks as Boyle's Law, Gay-Lussac's Law, Charles' Law, and Avogadro's Law are usefully regarded as subsets of the general gas law.
2. **Rates of Reactions (Kinetics)**
   a. The rate of a chemical reaction can be changed by varying the experimental parameters (T, P, concentration, surface area, catalyst, substance).
   b. The collision theory of reaction rates qualitatively explains the factors affecting reaction rates.
3. **Solutions and Stoichiometry**. Stoichiometry in solutions is conveniently based on attention to the molar concentrations (M) of reacting species. A chemical equation is the basis for interpreting and predicting quantitative relationships in chemical reactions (stoichiometry). Stoichiometric relationships are based on the mole concept.
4. **Acids and Bases**. Strong electrolytes (acids, bases, salts) dissociate completely in solution. By contrast, weak electrolytes dissociate only slightly.
5. **Thermochemistry**. A reaction that releases heat is termed an exothermic reaction. If the reaction absorbs heat, it is called an endothermic reaction.

RELATED SKILLS

1. **Chemical Skills**

   Write balanced net ionic equations.
   Write formulas of molecules, ions, radicals, and complexes.
2. **Mathematical Skills**

   Complete basic stoichiometric calculations.
   Use molar concentration units.
3. **Laboratory Skills**

   Use acid/base indicators.

PERFORMANCE OBJECTIVES

After completing their study of equilibrium, students should be able to:

1. state the conditions that result in some reactions reaching equilibrium while others do not.
2. predict the direction of shift in a system at chemical equilibrium, given a change in concentration, temperature, or pressure.
3. describe equilibrium and equilibrium shifts on the molecular level.
4. write the equilibrium expression for a system at chemical equilibrium.
5. calculate a value for *K* for a system at chemical equilibrium from suitable concentration data.
6. calculate the concentration of a reactant or product in a chemical equilibrium given the value of *K*, and all other reactant and product concentrations at equilibrium.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Concentration Effects

Introduction

In this laboratory activity you will investigate chemical reactions of the type A + B → C. You will then add several reagents to the reaction mixture to see the effect of each on the reaction.

Purpose

This laboratory activity will help you gain an understanding of a new type of chemical reaction.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Dispose of the chemicals as your teacher directs.

Procedure

1. Place about 50 mL 0.005 M KSCN, potassium thiocyanate, solution in a 100-mL beaker. Note the appearance of the solution.
2. Add about five drops 0.2 M $Fe(NO_3)_3$, iron(III) nitrate, solution to the KSCN solution and stir. Make notes about the appearance of the $Fe(NO_3)_3$ solution and of the combined solutions.
3. Fill each of five test-tubes about one-third full of the solution prepared in Step 2. Label one test-tube as the "standard" and place it in your test-tube rack.
4. In a second test-tube, put one drop of the $Fe(NO_3)_3$ solution. Mix and observe any changes that occur. Write your observations.
5. In the third test-tube, put a few crystals of solid KSCN (about the size of a small pea). Mix gently while observing and record your observations.
6. In the fourth test-tube, put one drop 0.1 M $AgNO_3$, silver nitrate solution. Mix and observe any changes that occur. Write your observations.
7. In the fifth test-tube, put a few crystals of solid NaF, sodium fluoride (about the size of a rice grain). Mix gently while observing and record your observations.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Write comparisons of the solutions in the five test-tubes.
2. Potassium ions (K^+) and nitrate ions (NO_3^-) are not active in any of the chemical reactions of this activity. Such "inactive" ions are sometimes termed "spectator ions." They are present because they are carried along with the "active" part of the chemical involved in the reaction. What are the active substances in the reaction between $Fe(NO_3)_3$ and KSCN?
3. The product of this reaction is $FeSCN^{2+}$. Write a balanced equation for the reaction studied in this laboratory activity.

4. What evidence is there for a chemical reaction between $Fe(NO_3)_3$ and KSCN?
5. Identify the cause of the color of the solution formed in Step 2.
6. Why does the color change when one drop of $Fe(NO_3)_3$ solution is added to the solution formed in Step 2?
7. Why does the color change when solid KSCN is added to the solution formed in Step 2?
8. What is the cause of the changes observed when the $AgNO_3$ solution is added? Write an equation to represent these changes.
9. Why does the color change when solid NaF is added to the solution?

Implications and Applications

Ammonia gas, NH_3, can be formed by the reaction of hydrogen gas, H_2, and nitrogen gas, N_2. The formation of ammonia is exothermic. An equilibrium is established according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

Predict the effects of each of the following on the equilibrium system. (Does the equilibrium shift to the right, to the left, or remain unchanged?)

1. Adding more nitrogen gas or hydrogen gas at constant volume and temperature.
2. Removing some ammonia gas at constant volume and temperature.
3. Heating the system at constant volume.
4. Decreasing the pressure of the system by changing the volume of the reaction vessel at constant temperature.

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LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Concentration Effects

Major Chemical Concept

This is intended as an introductory activity involving the concept of dynamic equilibrium. The ideas developed in this activity are: (1) chemical reactions do not always go to completion, and (2) a state of dynamic equilibrium can be established in a chemical system by the simultaneous formation of products from reactants and reactants from products. Dynamic equilibrium does not necessarily (or usually) occur when equal concentrations of reactants and products exist in the chemical system.

Level

While the laboratory activity itself is quite easily performed, the underlying notions are not basic level concepts. The activity fits well in either a general or honors level course.

Expected Student Background

1. Familiarity with observational evidence for chemical reactions.
2. Knowledge of common ions and ionic representations of equations.
3. Experience with double replacement reactions.
4. Some knowledge of kinetic molecular theory.

Time

Completing the activity and answering questions requires one 50-min class period.

Safety

No safety precautions beyond those that apply to normal chemical laboratory work need to be stressed for this activity. Some students may be concerned with the superficial resemblance between SCN^- and CN^-. Although SCN^- should be treated with the same respect as other chemicals, it does not have the level of toxicity of CN^-. Soluble chemicals should be washed down the drain with plenty of water. Solid chemicals should be disposed of in a solid waste jar.

Materials (For 24 students working in pairs)

60 Test-tubes, 18- x 150-mm
12 Test-tube racks
12 Beakers, 100-mL
12 Medicine droppers
0.2 M Iron(III) nitrate, $Fe(NO_3)_3$, small dropping bottle
0.005 M Potassium thiocyanate, KSCN, 50 mL
Potassium thiocyanate, KSCN, solid, 5 g
0.1 M Silver nitrate, $AgNO_3$, small dropper bottle
Sodium fluoride, NaF, solid, 5 g

Advance Preparation

$Fe(NO_3)_3$ solution: 8 g solid $Fe(NO_3)_3 \cdot 9H_2O$ in 100 mL solution. Carefully add 2-3 drops of concentrated nitric acid, HNO_3, to the solution. (*NOTE: The acid stabilizes the solution and represses the formation of a yellow color.*)

KSCN solution: 0.05 g solid KSCN in 100 mL solution. Include enough concentrated nitric acid (a few drops) to make the solution slightly acidic. (*NOTE: This solution may not keep. Check the solution before using.*)

$AgNO_3$ solution: 1.7 g solid $AgNO_3$ in 100 mL solution.

Small, centrally located containers of solid KSCN and NaF will be sufficient.

Pre-Laboratory Discussion

Students should be told that although the procedure is short and relatively simple, their detailed observations are essential in answering the questions and in understanding the concept being studied. No procedural instructions are needed except the location of the solutions and the solid KSCN.

Teacher-Student Interaction

While students are performing the activity, walk around the laboratory correcting errant procedures, and asking students for oral interpretations of their observations. This is not the time to explain the observations to students. Your questioning serves to focus students' thoughts on the system being observed. Assure students that there will be a class discussion of this laboratory activity after they have finished it.

Anticipated Student Results

The colorless KSCN solution and nearly colorless $Fe(NO_3)_3$ solution should form a brownish-red product. Adding either $Fe(NO_3)_3$ solution or KSCN crystals deepens the color of the solution. Adding $AgNO_3$ or NaF causes the color of the solution to fade.

Answers to Data Analysis and Concept Development

1. Students will write their observations in making the comparisons. General consensus should be obtained during the class discussion.
2. The active species are Fe^{3+} and SCN^-.
3. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$ (*NOTE: Students will probably not know to include the double arrow. This symbol can be introduced at the appropriate time in the post-laboratory discussion.*)
4. The evidence for a chemical reaction between $Fe(NO_3)_3$ and KSCN is the observed color change.
5. Some $FeSCN^{2+}$ product forms when $Fe(NO_3)_3$ solution is added to the KSCN solution. Although the $Fe(NO_3)_3$ solution may have been slightly colored, the deep color of the mixture of $Fe(NO_3)_3$ and KSCN solutions cannot be explained by dilution of $Fe(NO_3)_3$ solution with the colorless KSCN solution.
6. The color change is caused by the production of more $FeSCN^{2+}$. Formation of more $FeSCN^{2+}$ indicates that SCN^- was still available in the solution to react with Fe^{3+} from $Fe(NO_3)_3$.
7. The color changes when KSCN solid is added because SCN^- from the KSCN reacts with Fe^{3+} still present in the system. (*NOTE: The importance of the answers to Questions 5 and 6 is that neither reactant—Fe^{3+} or SCN^-—had been completely used up in forming product during the original mixing of the solutions. This key set of observations can serve as the focal point for introduction of the idea of dynamic equilibrium.*)

8. Two observations will be noted. First, Ag^+ reacts with SCN^- to form the precipitate AgSCN, decreasing the SCN^- concentration and shifting the equilibrium to the left. The second observation is the fading of the solution color as $FeSCN^{2+}$ concentration decreases. Focus class discussion on the fading color and its meaning. *(NOTE: The specific role of* Ag^+ *can be demonstrated by adding enough* $AgNO_3$ *to make the solution colorless, filtering the solution, and testing separate samples of filtrate with* Fe^{3+} *and* SCN^-*. The color should return with* SCN^-*, but not with* Fe^{3+}*, thus showing that* Ag^+ *removed* SCN^-*.) Students can be led to this conclusion by questions, trial, and error.*
9. As in Question 8, the color fades, indicating a decrease in $FeSCN^{2+}$ concentration. The evidence from the laboratory is that the F^- reacts with and removes the Fe^{3+}. This is the result of F^- forming a complex with Fe^{3+} to form $FeF_6{}^{3-}$. Focus on the meaning of the observable evidence in the class discussion. *(NOTE: Questions 8 and 9 can be used to develop the idea of reversibility of chemical reactions and the role of concentration in controlling reactions.)*

Answers to Implications and Applications

1. a. Shift the equilibrium toward products
   b. Shift the equilibrium toward products
   c. Shift the equilibrium toward reactants
   d. Shift the equilibrium toward reactants

Post-Laboratory Activities

Part B of *Laboratory Activity 2: Temperature Effects* can be combined with this activity if there is enough time. If this activity is done, tell students to save any excess solution made in Procedure 2 to use in *Laboratory Activity 2*.

After students have had time to prepare answers to the questions, lead a class discussion on the laboratory activity. In this discussion it is important to establish first that all student groups have compatible observations of the systems. Discuss any discrepant observations through questioning to clear up any problems. If students are adamant about observations that differ, do a quick demonstration to gain consensus.

Students may suggest that the reaction is a double displacement (*aka.*, double replacement or metathesis) reaction between potassium thiocyanate and iron(III) nitrate, according to: $3\ KSCN + Fe(NO_3)_3 \rightarrow Fe(SCN)_3 + 3\ KNO_3$. However, both products suggested by this equation would be soluble and ionic, resulting in identical ionic reactants and products (show this using a net ionic equation); thus such a prediction would not, by itself, account for the observations. If a precipitate had formed, there would be an argument in favor of the double displacement reaction. Of course, some sort of chemical reaction *did* occur as documented by the color change.

The formation of the complex ion $FeSCN^{2+}$ may cause some difficulty for students. It could be explained that the Fe^{3+} ion attracts the SCN^- ion strongly enough to hold them together as an ion. Actually, the chemical reaction is not the important focus of the activity. In fact, this laboratory activity could be carried out equally well by labeling the reactants as 'A' and 'B' and the colored product as 'C'. All of the same logic can be used to develop the ideas of the activity.

A discussion of the chemistry of the reaction can be done by using the questions as a discussion outline. As stated earlier, answers to Questions 6 and 7 permit you to suggest to students that it is possible for a chemical reaction to occur so that the final system contains *all* reactants and products simultaneously.

Pose a question about whether it is reasonable to accept the idea that products (in this reaction the product is $FeSCN^{2+}$) could change chemically back to reactants, as well as reactants changing chemically to form products. If students agree to such a possibility, ask them to offer an explanation for such a phenomenon. When a satisfactory explanation has been obtained, you can insert the double arrow in the chemical equation and explain that it designates to chemists that the system is reversible, that is, that it contains all reacting species.

Student laboratory observations can be used to establish the idea that this constantly changing system (on the molecular level) is still able to achieve constant concentrations of reactants and products (as observed by the constancy of the colors of the solutions).

The darkening of the solution when more of either reactant is added can be used (either now or later) as an example of LeChatelier's principle. You may decide that this is the best place to introduce the idea of LeChatelier's principle, or it might be better to address this principle after completing *Laboratory Activity 2* (see *Extensions*).

Extensions

1. Temperature effects on equilibrium point of a system (see *Laboratory Activity 2*).
2. Pressure effects on the equilibrium point of a gaseous system.

Assessing Laboratory Learning

Questions

1. Sodium chloride, NaCl, has a solubility of approximately 36 g/100 mL water. If 45 g of NaCl were added to 100 mL of water, 36 g would dissolve as Na^+ and Cl^- ions, but 9 g of solid NaCl would remain. Explain how this system could involve a dynamic equilibrium between solid NaCl and dissolved ions. *[Because the water molecules and dissolved ions are in constant motion, Na^+ and Cl^- ions could deposit on the NaCl solid, but for every pair of ions depositing on the solid, another pair of ions would go from the solid to the dissolved state.]*
2. What effect would adding 5 mL of KNO_3 solution to your "standard" test-tube (see Step 3) have on the test-tube solution's color? Note that a water solution of KNO_3 is colorless. *[The color of the "standard" solution would be less intense, due to dilution, but added KNO_3 would not cause a chemical change. It contains K^+ and NO_3^- ions that were "spectators" in the reaction.]*
3. Explain why an open beaker with zinc metal, Zn, and hydrochloric acid, HCl, will not establish chemical equilibrium. The products of the reaction of zinc metal and hydrochloric acid are hydrogen gas, H_2, and zinc chloride, $ZnCl_2$, solution. *[The system will not achieve equilibrium because a product—hydrogen gas—leaves the system. In order for dynamic equilibrium to be established, all products and reactants must remain in the system.]*

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: Temperature Effects

Introduction

In this laboratory activity you will study two chemical systems and observe the effect of temperature changes on them: (1) the aqueous ammonia system and (2) the Fe^{3+}/SCN^- system first studied in *Laboratory Activity 1*.

Purpose

To determine the effect of temperature on chemical systems.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. *CAUTION: The test-tube will be hot after heating. Be sure to use a test-tube holder.*
3. Concentrated ammonia solution has a strong odor. Avoid breathing the ammonia fumes. Be careful not to spill any concentrated ammonia solution on yourself. If you do spill any, wash the area with large amounts of water and notify your teacher.
4. Dispose of the chemicals as your teacher directs.

Procedure

Part A

1. Place about 400 mL distilled water in a large beaker.
2. Add one drop concentrated ammonia solution. Stir well.
3. Fill two large test-tubes half full of this solution.
4. Add one drop phenolphthalein indicator to each test-tube. The solution should be pink, but not dark pink (see teacher-made solution for exact color).
5. Gently heat one of the test-tubes over a burner until the solution begins to boil. Reserve the other test-tube as a "standard" for comparison. Record your observation of any changes that occur. Compare the heated solution with that of the unheated "standard" solution.
6. Let the tube cool for a few seconds, then place it in a stream of cold water. Record any changes that occur.

Part B

1. Put about 50 mL 0.005 M KSCN, potassium thiocyanate, solution in a 100-mL beaker. Note the appearance of the solution.
2. Add about five drops 0.2 M $Fe(NO_3)_3$, iron(III) nitrate, solution to the KSCN solution and stir. Make notes about the appearance of the $Fe(NO_3)_3$ solution and the combined solution.
3. Fill each of three test-tubes about one-third full of the solution made in Step 2. Label one test-tube as the "standard" and place it in your test-tube rack.
4. Place one of the test-tubes in a boiling water bath for 5 min. Place a second test-tube in a salt-ice water bath for 5 min. Compare the solution in each bath with your "standard" solution at room temperature.
5. Thoroughly wash your hands before leaving the laboratory.

Data Analysis And Concept Development

1. What ion accounts for the pink color of the aqueous ammonia solution?
2. Write a chemical equation for the reaction between ammonia and water resulting in the ion identified in Question 1.
3. What evidence is there that a chemical change occurred when the test-tube was heated? Write a chemical equation for this chemical change.
4. What effect did cooling the solution have on the aqueous ammonia solution? Write a chemical equation for this chemical change.
5. Is the reaction involved in Question 4 exothermic or endothermic? How do you know?
6. Write a net ionic equation for the reaction between iron(III) nitrate and potassium thiocyanate.
7. Analyze the equation you wrote in Question 6 in a manner similar to that of the aqueous ammonia system and determine whether this reaction is exothermic or endothermic.
8. Generalize about the effect of heat on reversible chemical reactions.

Implications and Applications

1. Why would the aqueous ammonia reaction not work well if too much ammonia were added?
2. Discuss how a change in temperature of a liquid solvent affects the solubility of a solid solute.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: Temperature Effects

Major Chemical Concepts

This activity is designed to develop the concept that a change in temperature can affect the equilibrium position of a chemical system.

Level

Basic, general or honors students

Expected Student Background

General knowledge of solutions and concentrations, formula writing, equation writing, balancing equations, effect of indicators in a solution, and acids and bases in solution.

Time

One 50-min for the laboratory activity and the discussion in which the concept is developed from the observations.

Safety

See safety suggestions in *Student Version*.

Materials (For 24 students working in pairs)

12 Beakers, 600-mL
36 Beakers, 100-mL
12 Burners
12 Test-tube holders
48 Test-tubes, 18- x 150-mm
12 Test-tube racks
12 Medicine droppers

Consumables (For 24 students working in pairs)

Phenolphthalein, in dropper bottle
Concentrated NH_3, ammonia, small dropper bottle (in Procedure A, two drops of dilute NH_3 can be used.)
Ice
0.2 M Iron(III) nitrate, $Fe(NO_3)_3$, small dropper bottle (see *Activity 1*)
0.005 M Potassium thiocyanate, KSCN, 60 mL (see *Activity 1*)

Advance Preparation

It is advisable to prepare a solution of the concentrated ammonia and phenolphthalein, that shows the desired color. Display the desired color of the solution to students before they start the laboratory procedure. Directions for preparation of the other solutions are in *Laboratory Activity 1*.

Pre-Laboratory Discussion

A discussion of the effect of indicators in basic and acidic solutions may be helpful to students. You may want to do *Part A*, Steps 1-3, as a class demonstration, and then make the excess ammonia solution available to students to complete the rest of the activity.

Teacher-Student Interaction

During the laboratory activity, it is advisable to move from group to group to insure that students have obtained the desired color with the phenolphthalein indicator. Have students look down the tube for a better color comparison. Make sure they do not look down the tube while heating it.

When students have gathered the data, have them attempt to write a chemical equation for what happened. They can be led to this equation by answering the questions in the activity. Many students, however, may need the class discussion to develop the equation unless they learned about the interaction of acids with water in previous acid-base studies.

Anticipated Student Results

The pink color of the aqueous ammonia solution should disappear when the solution is heated. The pink color returns when the solution is cooled. The color of $FeSCN^{2+}$ fades as the solution is heated. Cooling reverses this effect.

Answers to Data Analysis and Concept Development

1. The phenolphthalein is an indicator for base. The pink color indicates the presence of hydroxide ion in the solution.
2. The water hydrolyzes the ammonia according to the equation:

   $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

   Students will probably not indicate the reaction as an equilibrium until reversibility is established in later questions.
3. The fading of pink color indicates a decrease in hydroxide ion concentration. This evidence for the disappearance of a reactant indicates a chemical reaction. The reaction is the reverse of the reaction of Question 2:

   $$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$
4. The re-emergence of the pink color indicates an increase in hydroxide ion concentration. It also establishes this reaction as reversible (equilibrium):

   $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
5. Exothermic. Heat is absorbed by the products to reform reactants and thus shift the reaction to the left. This is consistent with what is observed:

   $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) + \text{Heat}$$
6. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$ (See discussion for *Laboratory Activity 1.*)
7. The reaction is exothermic. Since the color (due to the product $FeSCN^{2+}$) fades when the solution is heated, heat is absorbed by the product as the reaction shifts to the left:

   $$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) + \text{Heat}$$
8. Heat can shift the equilibrium position by being absorbed by reactants (if the reaction is endothermic) or products (if the reaction is exothermic), causing the added heat to be partially consumed in the reaction.

Answers to Implications and Applications

1. If the ammonia concentration is too high, the added heat may not lower the hydroxide ion concentration enough to change the color due to phenolphthalein.

2. As a rule of thumb, increasing the temperature of a solid/liquid mixture will increase the solubility of the solid. This is true because most dissolution processes of solids in water are endothermic. (There are exceptions. Increasing the temperature of a gas/liquid solution will decrease the solubility of the gas because the entropy factor is much more important in gaseous systems.)

Post-Laboratory Discussion

Use the "Data Analysis and Concept Development" questions as the basis of a discussion to develop the ideas of temperature effects on systems at equilibrium.

Extensions

1. Have students predict the effect that cooling would have on a system at equilibrium. After predictions are made, perform a laboratory activity in which the solution is cooled.
2. Possible Laboratory Activity: Boil 200 mL cold, saturated $CoCl_2(aq)$, cobalt(II) chloride solution. The cherry red solution turns blue. Pour the solution into a 15- x 60-mm test-tube. Place the lower quarter in salt-ice bath and heat the upper portion. The lower end becomes red, while the upper portion becomes blue (see *Demonstration 2*).

Assessing Laboratory Learning

Questions

1. What is a reversible reaction? *[A reaction where products can recombine to form reactants.]*
2. Compare the rates of forward and reverse reactions for a chemical system at equilibrium. *[Forward rate = Reverse rate]*
3. How is chemical equilibrium related to a reversible reaction? *[A reversible reaction is an example of chemical equilibrium.]*
4. What is chemical equilibrium? *[Behavior of a chemical reaction where forward and reverse reactions proceed at the same rate.]*
5. Using Le Chatelier's Principle, explain the effect of adding heat to a system at equilibrium. *[The system will respond by favoring the reaction that counteracts the heat increase; the endothermic reaction predominates.]*
6. Present a demonstration in which an equilibrium is shifted due to a change in temperature. Have students write an equation for the reaction, and explain the shift in equilibrium [*e.g.*, *Demonstration 1* based on $2NO_2(g) \rightleftharpoons N_2O_4(g)$].

DEMONSTRATIONS

Demonstration 1: $2NO_2(g) \rightleftharpoons N_2O_4(g)$ and Temperature

Purpose

To demonstrate the effect of temperature on a system at equilibrium.

Materials

Hot water bath
Ice water bath
3 $NO_2(g)$-filled tubes
Dry ice/acetone bath (optional)
Overhead projector

Safety

No special precautions are necessary other than those given in the directions.

Procedure

Obtain NO_2/N_2O_4 (nitrogen dioxide/dinitrogen tetroxide) gas tubes from an educational scientific supply house (*e.g.* ,Temperature Equilibrium Tubes, Sargent-Welch #4426).

Place one tube into a beaker of hot water 70 to 80 °C, one tube into a beaker of ice water (alternative: a dry ice/acetone bath; it will turn the gas colorless), and leave one tube at room temperature. Place all three tubes on an overhead projector and ask students to make observations. Write the equilibrium equation on the board:

$$\underset{\text{Brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{Colorless}}{N_2O_4(g)} + \text{Heat}$$

Ask students to use LeChatelier's principle to account for their observations.

Demonstration 2: $2NO_2(g) \rightleftharpoons N_2O_4(g)$ and Pressure

Purpose

To demonstrate the effect of pressure on a system at equilibrium.

Materials

Glass syringes, 30-mL
Plastic syringe cap
Nitrogen dioxide, $NO_2(g)$

Safety

Care must be taken to contain the NO_2 gas, preventing it from escaping into the room.

Procedure

In a hood collect some NO_2 in a syringe ($Cu + HNO_3$ (conc.) produces NO_2) by air displacement. Seal the syringe with a plastic syringe cap so no gas can escape. Firmly and rapidly press on the syringe to compress the gas as much as possible. At first the NO_2 gas appears darker (increased concentration) and then should fade (equilibrium shift). Demonstrate this reaction for individual students or small groups, since it may be hard to see. Write the following equilibrium equation:

$$\underset{\text{Brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{Colorless}}{N_2O_4(g)}$$

Discuss how increased pressure should shift the equilibrium to the right, lessening the color.

Demonstration 3: Temperature Effects on Cobalt Complexes

Purpose

To demonstrate the effect of temperature on a system at equilibrium.

Materials

Cobalt(II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$, (9.5 g per 100 mL solution)
Concentrated HCl (hydrochloric acid), 100 mL
Hot plate
Ice water bath
3 Beakers, 250-mL

Safety

Since the solution is highly acidic it should be neutralized with sodium bicarbonate before disposal and flushed down the drain.

Procedure

Pour 100 mL $CoCl_2$ solution into a 250-mL beaker; add concentrated HCl until the solution changes color (pink to blue). This may take considerable HCl (about 100 mL). Divide the solution into three beakers. Place one on a hot plate, one in an ice bath, and the third at room temperature. Have students explain the colors in terms of the following equation:

$$\text{Heat} + [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Demonstration 4: Rubber Band Equilibrium

Purpose

To demonstrate the effect of temperature on a physical equilibrium system.

Materials

Heavy rubber band
Hooked weights (100-500 grams depending on rubber band)
Ringstand and ring
Hair dryer
Meter stick

Safety

No special precautions are necessary.

Procedure

Suspend the weight from a rubber band attached to a ring stand. Put a meter stick next to the weight so that its distance from the table top can be measured. Discuss this system as an example of a physical system in static equilibrium. Ask students to predict what will happen if the rubber band is heated. Heat the rubber band with a hair dryer and measure its distance from the table. Allow it to cool and measure again.

Heated rubber band will be shorter than cooled rubber band due to entropy. Heating the system causes the ordered orientation of the molecules to become disordered. In the three dimensional system the rubber band becomes shorter.

GROUP AND DISCUSSION ACTIVITIES

Counterintuitive Examples, Discrepant Events

1. In a way, equilibrium systems are themselves discrepant events. The presence of all reactants and products in a reaction vessel is not expected by students who have generally been exposed earlier only to reactions that "go to completion."
2. Students sometimes get the idea that higher temperatures drive reactions towards completion. If dissolution is treated as an equilibrium (Solute + Solvent $\rightleftharpoons$ Solution), for example, increasing the temperature is thought to increase the concentration of the solution. Although this is most often true with solid/liquid combinations, there are exceptions (*e.g.*, Li_2SO_4). The solubility of NaCl is hardly affected by temperature at all. The solubility of a gas decreases with increased temperature. Opening a warm can of soda pop amply demonstrates this fact (see also Demonstration 2 in *Solubility and Precipitation* module).
3. Solubility equilibria are an excellent chance to challenge student ideas about physical *vs.* chemical changes. Ask students if a reaction resulting in a precipitate is a physical or chemical change [$M^+(aq) + A^-(aq) \rightarrow MA(s)$]. Then ask if the dissolution of an ionic salt is a physical or chemical change [$MA(s) \rightarrow M^+(aq) + A^-(aq)$]. Then show them that both reactions can be represented as one equilibrium reaction.

Pictures in the Mind

These diagrams represent molecular activity during a reversible reaction. Figure 1 is just one example from the *Teacher's Resource Manual*, Concept Mastery section; *Chemistry: the Study of Matter*, Prentice-Hall, Dorin, Demmin, and Gabel, pp. CM-31 and 32. Have students label each drawing. Which drawing(s) represent the system at equilibrium (B and C) and which represent the system not at equilibrium (A and D)?

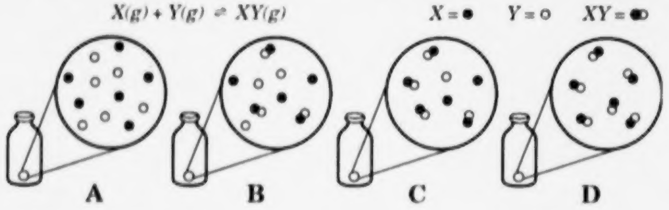


Figure 1. Pictures in the Mind.

Analogies and Metaphors

1. In a football game, the number of players on the field is constant although exchange of players (substitution) changes actual persons.
2. **Connected fish bowl analogy**. Two fish tanks are connected by a tube large enough to allow passage of fish. A number of fish are placed in one of the tanks. At equilibrium, the number of fish in each tank will eventually become unchanged.
3. Two jugglers analogy.

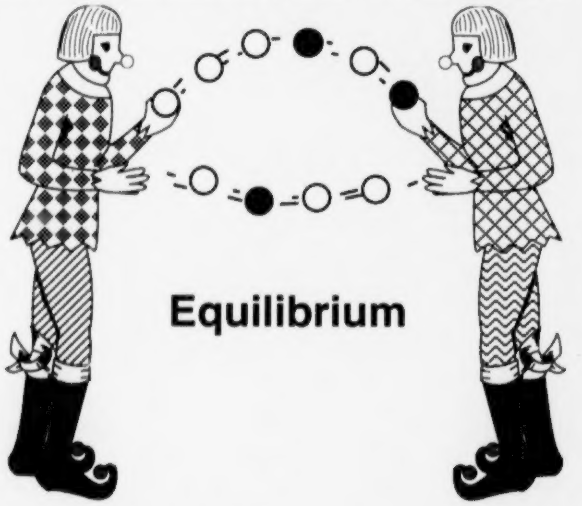


Figure 2. Two jugglers analogy.

4. Drinking fountain line:
   (a) Ten students waiting in line to get a drink of water on a hot day. As each gets a drink, the same student reenters the line (equilibrium in a closed system). (b) Same situation as "a," except as each student gets a drink and leaves, a new student enters the line (steady-state in an open system).
5. Picture a number of horses and wranglers in a corral. As each wrangler mounts a horse, the wrangler is bucked off. The equilibrium is:

   Horse + Wrangler $\rightleftharpoons$ Mounted wrangler

   Consider the effect (a la LeChatelier) of adding horses or wranglers.

Key Questions

1. Predict the direction of shift in a chemical equilibrium system given changes in concentration, temperature, and pressure. *[Answer this question by applying LeChatelier's Principle.]*
2. State the conditions that result in some reactions reaching equilibrium while others do not. *[All reactants and products of a chemical reaction must be present and in contact in order for an equilibrium state to be reached.]*
3. Describe equilibrium and equilibrium shifts at the molecular level. *[Use ideas of collision theory to answer this question.]*
4. Determine a value for *K* for a chemical equilibrium system from concentration data. *[See the discussion on Problem Solving in* Tips for the Teacher.*]*
5. Determine the concentration of a reactant or product in a chemical equilibrium system given the value of *K*. *[See a general chemistry text for the problem solving skills needed.]*
6. Determine the equilibrium expression for a chemical equilibrium equation. *[See the discussion on Problem Solving in this module.]*

Other

1. **Have students write essay answers to questions about Pictures in the Mind** (see examples in *Pictures in the Mind*).

   Examples of questions:

   a. Tell whether each picture represents a system in equilibrium.

   b. Explain your answer for each picture.

2. **Simulation**. Have students set up a factory to produce ammonia according to the Haber Process (see *Industrial Inorganic Chemistry* module). Include following steps.

   a. Invent process: $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$

   b. Develop ideal conditions (temperature and pressure).

   Raising the temperature favors the endothermic reaction (the reverse reaction) in which the rise in temperature is counteracted by the absorption of heat. Increasing the pressure favors the forward reaction in which four gas molecules are converted to two gas molecules.

   c. Develop how conditions will be met in the factory.

   Gases are compressed to high pressures; thus the yield of ammonia is increased even though high temperature is maintained to make the reaction come to equilibrium quickly. (At 500 °C, yield of ammonia increases from 0.1% to 47% if pressure is increased from 1 atm to 700 atm.)

   d. Invent need for a catalyst.

   A catalyst needs to be used to make the reaction fast enough.

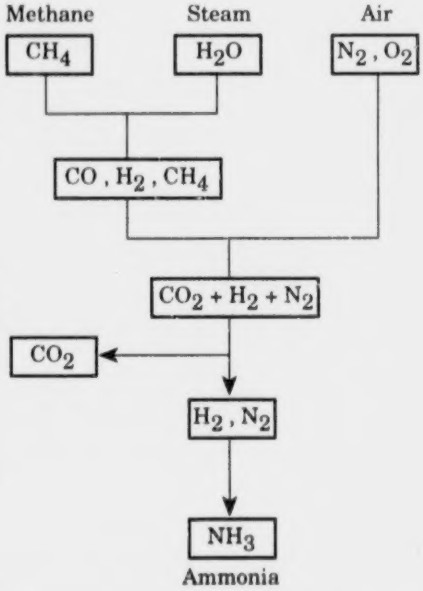


Figure 3. Steps of the Haber Process.

TIPS FOR THE TEACHER

Language of Chemistry

Key Words in LeChatelier's Principle

equilibrium the state of a chemical system in which the rate of product formation equals the rate of reactant formation.

stress refers to upsetting an established equilibrium system by adding more of a reactant or product to the system, or by changing reaction conditions such as temperature or pressure.

minimize means that a stressed equilibrium will respond to establish a new equilibrium state that reduces the added stress.

shift means that the adjustment of a stressed equilibrium system will result in the formation of more product (called a shift to the "right") or the formation of more reactant (called a shift to the "left").

Common Student Misconceptions

1. **"Reactions always go to completion."**

   The way we write chemical equations could imply that reactants completely become products. This is not necessarily true, especially in systems that establish equilibrium. The double reaction arrows $\rightleftharpoons$ serve to illustrate the fact that both reactants and products remain in a system at equilibrium.

2. **"Reactions at equilibrium have equal concentrations of reactants and products."**

   Actually, this is seldom the case at equilibrium. Values of equilibrium constants indicate the extent to which reactants form products. Large values represent reactions that go farther to the right before equilibrium is established.

3. **"Reactions at equilibrium have stoichiometrically related concentrations."**

   Some students think that the amounts of reactants and products in a reaction at equilibrium are fixed by the coefficients of the equation. The coefficients fix the relative amount that will react, not the amounts that are present.

4. **"Equilibria are static."**

   It is common for students to see chemical equilibrium as a static balance rather than a dynamic balance between forward and reverse interactions of molecules.

5. **"The right and left sides of an equation represent different regions of the reaction vessel."**

   A chemical equation is simply a formalized way to depict the chemical system, and the terms "left" and "right" refer *only* to the written equation. There is no "sidedness" to the chemical system itself. Reactants and products are intermingled.

Problem Solving

1. If equilibrium constants are calculated, skills associated with the mathematical solution of the problem need to be stressed.

Example: Given that $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, and that the molecular concentrations of reacting species at equilibrium were $[H_2] = 0.221$ M, $[I_2] = 0.221$ M, and $[HI] = 1.563$ M. Then:

$$K_{eq} = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K_{eq} = \frac{(1.563\ \text{mol/L})^2}{(0.221\ \text{mol/L})(0.221\ \text{mol/L})}$$

$$K_{eq} = 50$$

2. From a general problem solving point of view students will need to develop strategies for determining equilibrium shifts utilizing LeChatelier's Principle and changes in temperature, pressure and concentration.

$$K_{eq} = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

Addition of nitrogen gas, hydrogen gas, or ammonia gas to this system will cause shifts in the equilibrium. With heat on the right side of the equation, we see that the formation of ammonia is exothermic. Addition of heat to the system will cause a shift to the left. Increasing pressure on the system will cause a shift to the right because the smaller number of product particles would cause less pressure than the larger number of reactant particles, thus relieving the stress on the equilibrium caused by the increase in pressure.

3. Students are sometimes confused by shifts in equilibrium caused by temperature changes. If heat is represented as a product (in an exothermic reaction) or a reactant (in an endothermic reaction) in the equation for the reaction, then a change in temperature adds or takes away heat from the system. In this way, temperature is treated in the same way as increases or decreases in concentration. For example:

$$A + B \rightleftharpoons C + \text{Heat}$$

An increase in temperature increases the quantity of heat (a product), thus shifting the reaction to the left.

HISTORY: ON THE HUMAN SIDE

1. **Fritz Haber and The Haber Process**. Fritz Haber, a German, received the Nobel Prize in chemistry in 1919 for synthesizing ammonia from its elements, nitrogen and hydrogen. Haber's life was filled with ironic tragedies. His motivation for developing a method for producing ammonia was to make possible unlimited supplies of fertilizer to replace the limited supply of natural fertilizers (from nitrate deposits in Chile). Many were predicting massive starvation in Europe unless this was done. Ironically, ammonia could also be used to produce explosives. As a result Germany was able to produce its own explosives during World War I despite a blockade of nitrate compounds by the Allied powers.

Haber was a patriot and German nationalist and as a consequence threw himself into the German war effort. One of his contributions was development of mustard gas, a horrible instrument of war that caused much suffering. Ironically, many compounds related to mustard gas have been use as anti-cancer agents, ultimately saving lives. The Nobel Prize he received was criticized by British, American, and French scientists.

A final irony in Haber's life occurred when he was driven out of Germany before World War II because of his Jewish ancestry, despite his proven loyalty to his country.

2. **Who was LeChatelier?** Henry Louis LeChatelier (1850-1936) was a French chemist who conducted research on chemical equilibrium, the combustion of gaseous mixtures on metals, alloys, *etc.* He enunciated his principle dealing with the equilibrium of a system as a result of study of the industrial production of iron. Iron oxides were heated with carbon monoxide in a blast furnace to produce iron and carbon dioxide. However, carbon monoxide was also found in the products. This puzzling finding was explained in various ways. After researching the problem, LeChatelier proposed the idea of a reversible reaction to account for the carbon monoxide.

HUMOR: ON THE FUN SIDE

1. Bumper Sticker (American Chemical Society, Office of Precollege Science, Room 806; 1155 Sixteenth Street, N.W., Washington, DC 20036)

   Old Chemists Never Die . . . . They Just Reach equilibrium

   Δ
2. Student response on exam:

   LeChatelier's Principle is, if a strain is applied on a substance, the substance will try to assume the most comfortable condition.
3. The meaning of "reversible reaction"? *Starting material recovered. (CHEM 13 NEWS, October 1970, p. 193)*
4. Word Search (see *Appendix* for master copy)

C	P	R	~~E~~	~~R~~	~~U~~	~~S~~	~~S~~	~~E~~	~~R~~	~~P~~	L	R	X	I	S	Z
A	N	R	X	C	S	I	X	Y	I	R	Y	B	A	Z	K	X
~~A~~	~~M~~	~~M~~	~~O~~	~~N~~	~~I~~	~~A~~	V	R	T	N	Y	W	I	X	M	G
L	S	F	T	C	D	Q	C	K	Z	A	F	A	U	N	U	B
N	N	O	H	F	Z	G	O	G	L	U	~~S~~	~~T~~	~~A~~	~~T~~	~~I~~	~~C~~
~~R~~	~~E~~	~~V~~	~~E~~	~~R~~	~~S~~	~~I~~	~~B~~	~~I~~	~~L~~	~~I~~	~~T~~	~~Y~~	I	N	R	P
Y	J	J	R	R	T	S	A	U	I	X	Y	M	L	S	B	A
Z	I	A	M	T	R	O	L	C	R	C	A	S	A	M	I	E
U	T	P	I	N	E	S	T	X	T	X	G	I	R	N	L	C
Y	D	E	C	A	S	V	I	F	V	W	R	E	K	Z	I	E
B	X	W	E	R	S	S	A	T	J	E	B	I	F	W	U	P
H	V	F	R	F	R	M	M	K	H	A	N	J	N	J	O	P
Z	J	~~R~~	~~E~~	~~I~~	~~L~~	~~E~~	~~T~~	~~A~~	~~H~~	~~C~~	~~E~~	~~L~~	B	I	E	L

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Change in the reaction conditions of an established equilibrium.

2. State of a chemical system such that the rates of formation of products and reactants are equal.
3. German chemist who synthesized Item 6 from nitrogen and hydrogen.
4. Characteristic of an equilibrium system.
5. Factor that can cause a shift in a gaseous system at chemical equilibrium.
6. Substance formed in the nitrogen plus hydrogen gaseous equilibrium.
7. Type of reaction in which heat is absorbed by products to reform reactants.
8. Metal in complex responsible for pink-to-blue color change as temperature changes.
9. Balanced see-saw represents this type of equilibrium.
10. French chemist for which a famous principle of equilibrium is named.

Answers: 1. STRESS 2. EQUILIBRIUM 3. HABER 4. REVERSIBILITY 5. PRESSURE 6. AMMONIA 7. EXOTHERMIC 8. COBALT 9. STATIC 10. LECHATELIER

5. See cartoons at end of module.

MEDIA

1. *Chemistry: Reaction Rates and Equilibrium,* 23 min. video available from Coronet/NTI Film and Video, 108 Wilmot Road, Deerfield, IL 60015; (800) 621-2131; (708) 940-3640 (FAX).
2. *Equilibrium*, CHEM Study film/video available from Ward's Natural Science Establishment, Inc., 5100 West Henrietta Road, P.O. Box 92912, Rochester, NY 14692-9012; (800) 2660.
3. *Introduction to Chemical Equilibrium*, Chem 101 Series, University of Illinois Visual Aids Service, 1325 South Oak, Champaign, IL 61820; (800) 367-3456.
4. Imperial Chemical Industries Ltd. *Laws of Disorder*, Pt 4: *Equilibrium: The Limit of Disorder*. ICI Film Library, Thames House North, Mill Bank London SW1P 40G. (Held at University of Minnesota, University Film & Video, 1313 Fifth St. SE, Minneapolis, MN 55414, 1-800-847-8241.)
5. TV Ontario: *Chemical Equilibrium*. Six 10-minute video programs with a guide covering various aspects of equilibrium. TVO Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516, 1-800-331-9566.
6. The *World of Chemistry* videotape "Number 14: Molecules in Motion." World of Chemistry Videocassettes. Annenberg/CPB Project, P.O. Box 1922, Santa Barbara, CA 93116-1922; (800) 532-7637; World of Chemistry Series, Atlantic Video, 150 South Gordon Street, Alexandria, VA 22304; (703) 823-2800 or QUEUE Educational Video, 338 Commerce Drive, Fairfield, CT 06430; (800) 232-2224. A secondary school version of this series is available from WINGS for Learning/SUNBURST, 101 Castleton Street, Pleasantville, NY 10570; (914) 747-3310; (800) 321-7511; (914) 747-4109 (FAX).

7. Software published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
   a. *Equilibrium Calculator*, by Robert D. Allendoerfer. Vol. VI B, No. 1, for IBM PS/2 PC-compatible computers.
   b. *Equilibrium Calculator*, by Robert D. Allendoerfer. Vol. I D, No. 1, for Windows/IBM PC.
8. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).
   a. For the IBM PS/2 PC-compatible computer: PC 2901 (Equilibrium simulation program where user inputs data; concentration of each species after each given increment is given numerically or as bar graphs until equilibrium is reached.)
   b. For the Apple II computer: AP 603 (same as PC 2901).
9. Metcalfe, H., *et al.* (1986). *Modern chemistry: Disk for equilibrium chapter.* New York, NY: Holt, Rinehart, & Winston.
10. Prentice-Hall: *Dynamic Equilibrium.* 4343 Equity Drive, P.O. Box 2649, Columbus, OH 43216.

Links/Connections

WITHIN CHEMISTRY

1. Two of the most dangerous pollutants in the exhaust from automobiles are nitric oxide (NO) and carbon monoxide (CO). In the presence of a Monel (a nickel-copper alloy) catalyst, the concentrations of these gases are reduced by the following equilibrium process:

   $$2NO(g)\ 2CO(g) \rightleftharpoons N_2(g) + CO_2(g)$$

   The equilibrium constants vary with temperature as follows:

K_p	10^{98}	$10^{96.2}$	$10^{64.2}$	$10^{52.8}$	$10^{43.6}$
T(K)	600	700	800	900	1000

   Is the reaction exothermic or endothermic? *(Exothermic)*

2. A proposed method for collecting solar energy involves the equilibrium process:

   $$2SO_3(g) + \text{Heat} \rightleftharpoons 2SO_2(g) + O_2(g)$$

   The sulfur trioxide is heated in a chamber to 800 °C by solar energy. The sulfur dioxide and oxygen are then transported to a low-temperature heat exchanger where they recombine to form sulfur trioxide and liberate heat. At 800 °C, sulfur trioxide is 56% dissociated when the total pressure is 3.00 atm or 304 kPa. K_p is 1.05 atm or 1.07×10^5 Pa or 1.07×10^2 kPa.

3. K_{sp} (solubility product constant), K_a (dissociation constant for acids), K_b (dissociation constant for bases), and K_f (formation constant for species, such as $FeSCN^{2+}$ in this module's *Laboratory Activity 1*).

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

1. Chemical processing plants, such as oil refineries and chemical manufacturing plants, work with chemical reactions that establish dynamic equilibrium. It is often true that much creative energy is expended to determine how to shift the equilibrium so that the desired product is produced in large quantity and at a reasonable cost. A good example of this problem is the synthesis of ammonia from the elements, according to the equation:

   $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

2. Stalactite/stalagmite growth is based on equilibrium involving calcium carbonate and carbonic acid. See the article in *ChemMatters* by David Tanis (February 1984, pp. 10-11, "Underground Sculpture").

TO THE CONTEMPORARY WORLD

Personal

1. The problem of the relationship between eating sugar and tooth decay should interest most students. Fermentation of sugar in the mouth involves an increase in H^+ concentration. Over a period of time, such as a night's sleep, increasing H^+ can shift the equilibrium between tooth enamel and the ions making up the enamel to the ion side of the reaction. The equilibrium is:

   $$\underset{\text{Tooth enamel}}{Ca_5(PO_4)_3OH(s)} \rightleftharpoons 5Ca^{2+}(aq) + OH^-(aq) + 3PO_4^{3-}(aq)$$

   Stress is put on this equilibrium by formation of HOH (H_2O) and/or HPO_4^{2-}, causing a net loss of solid enamel.

2. Carbon monoxide, a by-product of "incomplete" oxidation (burning) of hydrocarbons, poses a major pollution problem. It is dangerous to life because it binds to hemoglobin and therefore excludes oxygen. Hemoglobin is a complex molecule that transports oxygen in the blood system.

   The binding process can be represented by the equilibrium:

   $$\text{Hemoglobin} + O_2 \rightleftharpoons \text{Bound } O_2$$

   Because of a balance between the forward and reverse reactions, oxygen can be released where it is needed in the body. However, CO can also bind to hemoglobin:

   $$\text{Hemoglobin} + \text{CO} \rightleftharpoons \text{Bound CO}$$

   This equilibrium has a greater K_{eq} than the hemoglobin–O_2 reaction. Consequently the hemoglobin is not available to transport oxygen. The victim of CO poisoning suffocates.

3. Ozone in our upper atmosphere absorbs ultraviolet light from the sun according to the equilibrium:

   $$O_3(g) \overset{\text{UV}}{\rightleftharpoons} O_2(g) + O(g)$$

   The reverse action regenerates O_3, which can absorb more ultraviolet light. Chlorofluorocarbons have been used in aerosols and refrigerants. These substances can release chlorine radicals that destroy O_3 irreversibly. Scientists are concerned that increased levels of chlorofluorocarbons will migrate into the upper atmosphere and deplete the ozone supply, allowing larger quantities of potentially harmful ultraviolet radiation to penetrate to the earth's surface.

Community

1. **Field trips**. Control of equilibrium is a theme in many industrial processes. A visit to a local chemical industry might be a useful activity, although equilibrium probably should not be the only reason for the visit.
2. **Knowledgeable individuals**: industrial chemists, university chemists, physicians, and pharmacists

Societal

A visit to a chemical plant to see the contrast between laboratory-based chemistry and scaled-up chemistry might be useful. Again, the direct association with equilibrium is not the sole reason for such a visit.

Extensions

1. **Relate equilibrium to solubility**. Partially soluble salts (*e.g.*, AgCl, PbI_2, or $PbCl_2$) can be used to explore the equilibrium aspects of solubility and to determine values for K_{sp}. Two approaches can be used. (1) Put a weighed excess of the salt in a measured amount of water; stir; filter the undissolved salt from the liquid, dry and weigh the undissolved salt. From the difference in masses the quantity of dissolved salt can be determined. (2) Precipitate the salt from soluble ions (*e.g.*, AgCl from $AgNO_3$ and NaCl). Filter the precipitate, dry and weigh. Compare the mass with the stoichiometrically expected mass. The difference is the mass of dissolved salt.
2. **Relate equilibrium to buffer action**. The pH of various buffered systems can be studied. The acetic acid/acetate system can be studied by varying the relative concentrations of the two species.
3. **Quantitative treatment of equilibrium**. Two straightforward methods can be used to derive equilibrium constants. (1) Measure the pH of a serial dilution of acetic acid from 0.1 M to 0.0001 M. Use a pH meter (inexpensive battery-operated ones can be obtained from Fisher Scientific – 13-300-51). (2) Compare the relative conductivity of 0.01 M HCl (assume 100% dissociation) with the same concentration of $HC_2H_3O_2$. By assuming the percent dissociation is related to the relative conductivity, the K_a value of acetic acid can be determined. An inexpensive battery-operated conductivity apparatus can be obtained from Fisher Scientific (09-331-4). It comes in two ranges and is called a dissolved solids tester. You may need two ranges to do this test (100-19,900 mS and 10-1,990 mS).

References

Module developed by Michael Abraham, Donna Coshow, and William Fix, the Oklahoma team.

Most college general chemistry texts thoroughly treat equilibrium. Various aspects of equilibrium include: general equilibrium, weak acid and base behavior, aqueous equilibrium (buffer solutions and solubility product), and dissociation (or formation) constants for complexes.

Davenport, D. (1985, February). When push comes to shove: Disturbing the equilibrium. *Chem Matters, 3*(1), 14-15.

This is a brief discussion of Le Chatelier's Principle.

Goran, M. H. (1967). *The story of Fritz Haber*. Norman, OK: University of Oklahoma Press.

Lund, E. W. (1968). Activated complex—a centenarian? A tribute to Leopold Pfaundler. *Journal of Chemical Education, 45,* 125.

An historical account of the ideas of a pioneer in equilibrium theory.

Oesper, R. E. (1931). The scientific career of Henry Louis LeChatelier. *Journal of Chemical Education, 8,* 442-461.

Parker, S. P. (Ed.). (1987). *McGraw-Hill encyclopedia of science and technology* (6th Ed.). New York, NY: McGraw-Hill.

This is a very good reference source for discussion information or student research information on many topics relating to equilibrium. This set is available in many schools and public libraries.

Runquist, E. A., and Runquist, O. (1972). Passage of fruit flies through a hole, a model for a reversible chemical reaction. *Journal of Chemical Education, 49,* 534.

Slabaugh, W. H. (1967, November). Chemical equilibrium. *The Science Teacher, 34*(8), 61-66.

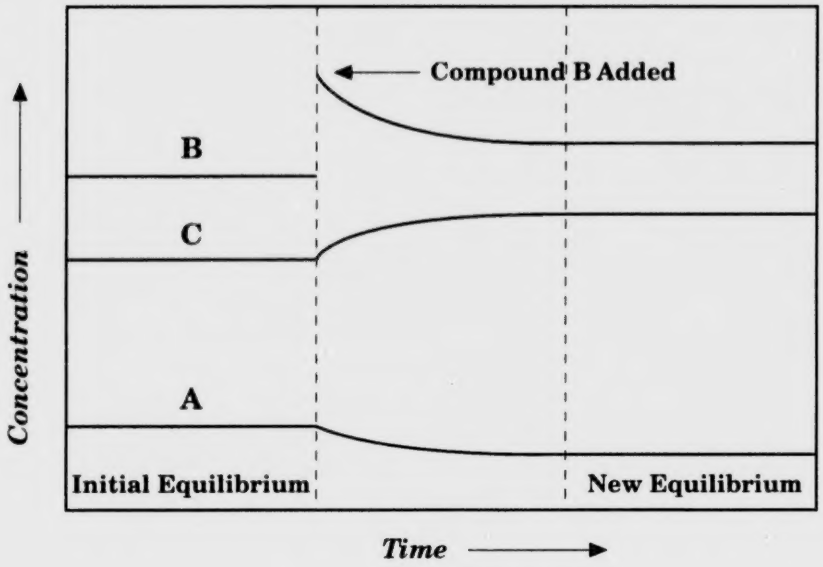
This is a brief discussion of equilibrium and how it is taught.

Appendix

- **Transparency Masters**
  1. Effect of Increasing Concentration on a Chemical Equilibrium System
  2. Word Search
- **Humor**

Effect of Increasing Concentration on a Chemical Equilibrium System

$$A + B \rightleftharpoons C$$



Word Search

C P R E R U S S E R P L R X I S Z
A N R X C S I X Y I R Y B A Z K X
A M M O N I A V R T N Y W I X M G
L S F T C D Q C K Z A F A U N U B
N N O H F Z G O G L U S T A T I C
R E V E R S I B I L I T Y I N R P
Y J J R R T S A U I X Y M L S B A
Z I A M T R O L C R C A S A M I E
U T P I N E S T X T X G I R N L C
Y D E C A S V I F V W R E K Z I E
B X W E R S S A T J E B I F W U P
H V F R F R M M K H A N J N J Q P
Z J R E I L E T A H C E L B I E L

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. **Change in the reaction conditions of an established equilibrium.**
2. **State of a chemical system such that the rates of formation of products and reactants are equal.**
3. **German chemist who synthesized Item 6 from nitrogen and hydrogen.**
4. **Characteristic of an equilibrium system.**
5. **Factor that can cause a shift in a gaseous system at chemical equilibrium.**
6. **Substance formed in the nitrogen plus hydrogen gaseous equilibrium.**
7. **Type of reaction in which heat is absorbed by products to reform reactants.**
8. **Metal in complex responsible for pink-to-blue color change as temperature changes.**
9. **Balanced see-saw represents this type of equilibrium.**
10. **French chemist for which a famous principle of equilibrium is named.**

MY REPORT TODAY IS ON CHEMISTRY SYMBOLS
THESE ARROWS INDICATE "DIRECTION OF REACTION"... UNLESS YOU'RE A COWBOY.. THEN THEY MEAN, "IF YOU DON'T DUCK, YOU'RE GONNA GET IT IN THE HEAD!"
HAHAHAHA!
OKAY, GETTING BACK TO CHEMISTRY..
9-26
SCHULZ

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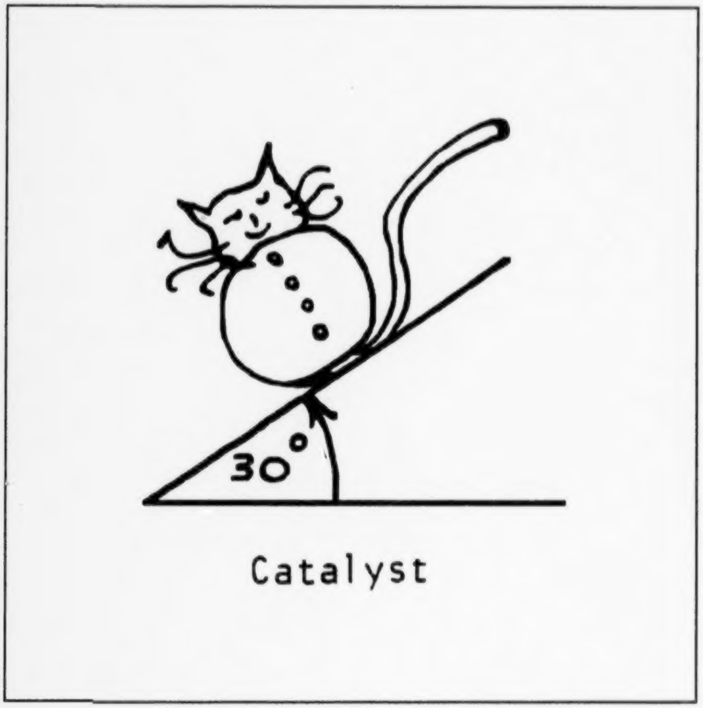
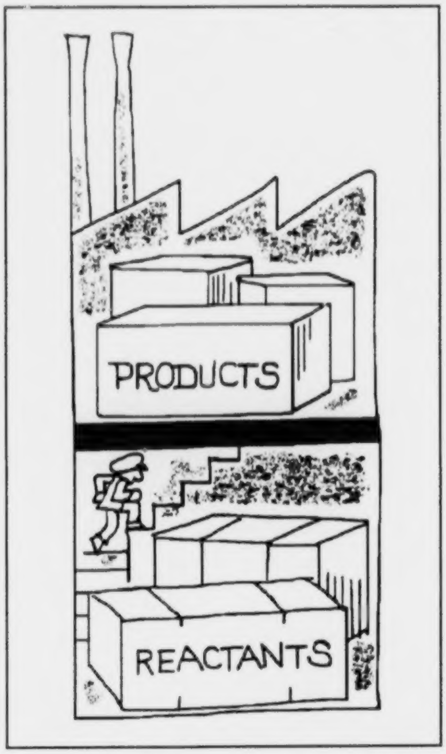


Copied with permission from CHEM 13 NEWS, October 1977, p. 15

WHY ARE YOU GRINNING LIKE THAT?
"THE DERANGED SCIENCE TEACHER'S THOUGHTS"
WHAT'S THAT ON YOUR HEAD?
WHEN SOMEONE TRIES TO CHANGE MY SYSTEM, I SHIFT INTO EQUILIBRIUM

CHEM 13 NEWS, February 1981, p. 10. Reprinted with permission.



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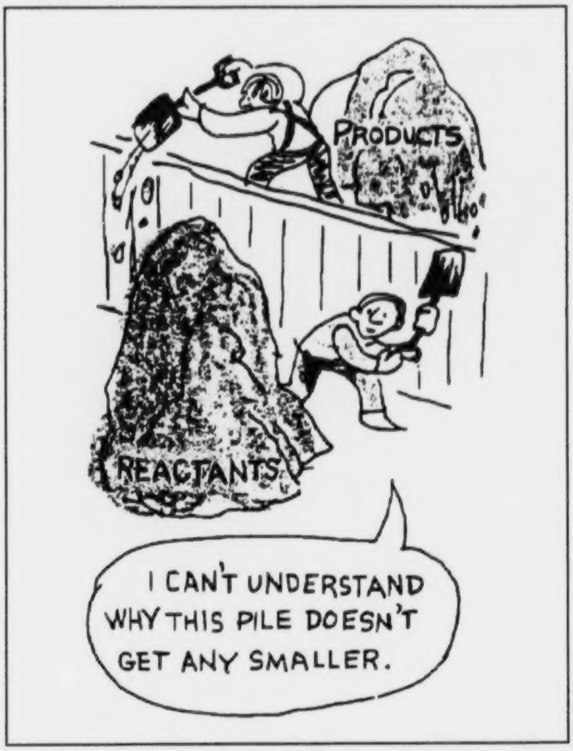
PRODUCTS
REACTANTS
I CAN'T UNDERSTAND WHY THIS PILE DOESN'T GET ANY SMALLER.

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A SourceBook Module

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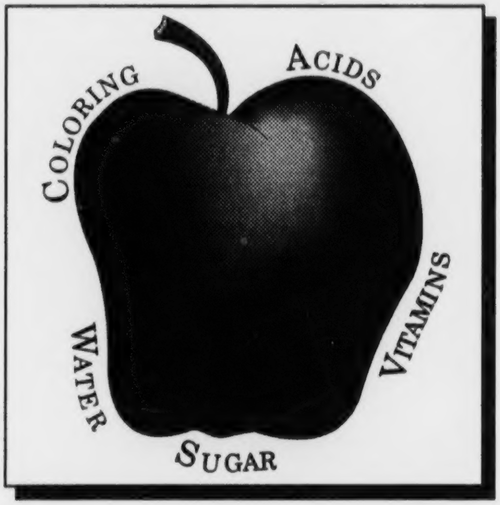
FOOD AND CHEMISTRY



ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

"What in the world *isn't* chemistry?" We often read or view statements leading the average person to believe that all chemicals are dangerous, that they should be avoided, and that "natural" substances are preferable to "chemicals." But every natural thing is made of chemicals: the food we eat, the air we breathe, the clothes we wear, and even our own bodies.

In this module, students will study some of the foods they eat and investigate how to use and buy the products they consume. Although no new concepts are introduced, many fundamental chemical concepts such as oxidation-reduction, acids and bases, and biochemistry are reinforced by the subject matter in this chapter. Students will see that chemicals are part of their daily nutrition and learn that "natural" products such as milk yield to analysis just like chemicals from the stockroom.

PLACE IN THE CURRICULUM

This module may be used at all levels of study. Some parts assume knowledge of fundamental concepts.

CENTRAL CONCEPTS

1. Not all chemical substances are bad for human consumption. Foods are essential for our existence.
2. Certain compounds and elements are essential for a balanced diet.
3. The body has certain nutritional requirements, and the foods we eat affect our health.
4. Labels on foods and other products are important in helping consumers understand the nature of the ingredients and additives used.

RELATED CONCEPTS

1. Oxidation-reduction
2. Solution properties
3. Basic organic chemistry
4. Nutritional needs
5. Protein chemistry

RELATED SKILLS

1. Good observational skills
2. Quantitative techniques

PERFORMANCE OBJECTIVES

After completing their study of food and chemistry, students should be able to:

1. know that foods are made of chemical substances.
2. describe some laboratory activities that can be done with everyday substances.
3. read and analyze some labels and determine the best buy in certain substances.
4. classify food additives (*e.g.*, acids, bases, sweeteners, preservatives) according to their properties.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Analysis of NaCl in Snack Food

Introduction

Table salt (sodium chloride, NaCl) is an important component of the human diet. Since too much salt may cause health problems such as high blood pressure or kidney and heart disease, "low salt" or "low sodium" foods have become popular and are readily available. Additionally, the Federal Government requires all food to be labeled with its nutritional components, including sodium. In this laboratory activity, you will determine the actual amount of NaCl in Fritos® snack food.

Prior to the laboratory, your instructor soaked a known amount of Fritos® in distilled water to dissolve the salt. You will be given the information about the mass of Fritos® used and the total volume of the solution obtained. You are to assume that all the salt from the Fritos® dissolved.

Purpose

To determine the mass of NaCl in a package of Fritos® using the Mohr chloride titration method.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Silver nitrate ($AgNO_3$) solutions stain skin and clothes; wash off immediately to prevent stains.
3. Potassium chromate (K_2CrO_4) is toxic if taken internally, and may irritate the skin. Wash off immediately to prevent skin irritation.

Procedure

1. Obtain from your instructor information about the mass of Fritos® used and the total volume of the solution. Record these values in your Data Table.
2. Fill the buret above the 50-mL mark with the $AgNO_3$ solution. Open the stopcock to fill the buret tip and remove the bubbles. Record the Initial Reading for the Blank analysis in the Data Table. (The buret level does NOT have to be at 0.0 mL.)
3. Blank titration: Using a pipette, transfer 10.0 mL distilled or deionized water into a 125-mL Erlenmeyer flask and add 20 drops chromate indicator. Titrate with the $AgNO_3$ solution to a pinkish-orange end point. Record the mL of $AgNO_3$ used. Repeat 2-3 times and average the values. A blank value of 0.2-0.3 mL is normal.
4. Sample titration: Using a pipet, transfer 10.0 mL Fritos® filtrate into a 125-mL flask and add 20 drops chromate indicator. Titrate with $AgNO_3$ until a pinkish-orange end point is reached. It should look almost like orange juice. Keep this titration flask for comparison with the next trial. Repeat Step 4 two additional times and record in the Data Table. If your results are not consistent (±0.5 mL), you should do additional sample titrations.
5. When you have completed the titrations, clean your buret as directed by your instructor. Remember that $AgNO_3$ stains the skin. Titration solutions should be disposed of as directed by your instructor.
6. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Average the blank titration values.
2. Average the sample titration values. Subtract the average blank value from the average sample value.
3. Using the ratio, $\frac{0.825\text{ mg NaCl}}{1\text{ mL AgNO}_3}$, calculate mg NaCl per gram of sample.
4. Calculate the mg NaCl in the entire package of Fritos®.
5. Calculate mg Na in the entire package.
6. How do your experimental values compare with the stated value on the label? Can you explain any discrepancy?

Data Table

		Trial 1	Trial 2	Trial 3
Blank Titration	Final:	______	______	______
	Initial:	______	______	______
	mL $AgNO_3$ Used:	______	______	______
	Average mL $AgNO_3$ used for the blank:		______ mL	
Sample Titration	Final:	______	______	______
	Initial:	______	______	______
	mL $AgNO_3$ Used:	______	______	______
	Average mL $AgNO_3$ used for the sample:		______ mL	
	Average mL $AgNO_3$ for Cl^- tritration (sample–blank):		______ mL	
	Mass of Fritos® used:			______ g
	Total volume of filtrate:			______ mL

Implications and Applications

1. Find the recommended level of sodium intake in the daily diet.
2. Examine a package of your favorite salty snack and find the mass of sodium listed. Calculate the mass of NaCl, and teaspoons of NaCl, assuming that one teaspoon of NaCl has a mass of approximately 6 g.
3. If someone has a family history of high blood pressure, stroke, kidney, or heart disease, what dietary changes would a physician recommend to that person with regard to salt intake?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Analysis of Sodium Chloride in Snack Food

Major Chemical Concept

Students will use the Mohr Chloride Titration method (see *Pre-Laboratory Discussion* Items 3 and 4) to determine the amount of sodium chloride in a snack food such as Fritos®.

Level

This activity is appropriate for all levels of chemistry classes.

Expected Student Background

Skills: Using a buret, pipet, and unit analysis calculations. **Concepts**: Solubility, averaging values of several trials in an analysis, using a "blank" in chemical analysis.

Time

40-50 min, if snack filtrate is prepared ahead of time.

Safety

Read the *Safety Considerations* in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

48 Erlenmeyer flasks, 125-mL
12 Burets, 50-mL
12 Pipets, 10-mL
12 Ringstands and buret clamps

Consumables (see *Advance Preparation*)

0.0141 M Silver nitrate, $AgNO_3$, 600 mL
12 dropping bottles 5% Potassium chromate, K_2CrO_4
Snack filtrate, 480 mL

Advance Preparation

1. Preparing the snack filtrate: Weigh out 20.0 g of crushed Fritos®; soak 24 hr in 600 mL distilled water; filter through thick cheese cloth, rinse, and bring total volume to 600 mL in a graduated cylinder. The solution will be cloudy. Record exact volume. Use pH paper to test pH of filtrate. If pH is below 7.0 or above 10.0, adjust with 1 M NaOH or 0.5 M H_2SO_4, respectively. The filtrate should be stored in a refrigerator. To prevent mold, add a few crystals of thymol or a few drops of Lysol disinfectant. *WORD OF WARNING: Pretzels are suitable, but potato chips and cheese-flavored snacks are difficult to filter.*
2. Solution preparation:
   a. $AgNO_3$ solution, 0.0141 M: Dissolve 2.40 g $AgNO_3$ (dried overnight at 140 °C) in chloride-free water and dilute to 1.00 L. Store in a brown bottle.
   b. K_2CrO_4 indicator solution: Dissolve 10 g K_2CrO_4 in a little distilled water. Add $AgNO_3$ solution until a definite red precipitate is formed. Allow to stand 18-24 hr, filter, and dilute filtrate to 200 mL with distilled water. Put into dropper bottles.

c. 1 M NaOH: Dissolve 4 g in distilled H_2O and dilute to 100 mL.

d. 0.5 M H_2SO_4: Dilute 3 mL 18 M H_2SO_4 to 100 mL—carefully!

e. 0.01 M NaCl: 0.06 g NaCl per 100 mL solution.

3. Assume that 1.0 mL $AgNO_3$ solution ≈ 0.825 mg NaCl

(0.0141 mol Ag^+ ≈ 0.0141 mol NaCl from equation.

$$0.0141 \text{ mol NaCl} \times \frac{58.5 \text{ g NaCl}}{\text{mol NaCl}} = \frac{0.825 \text{ g NaCl}}{\text{L}} = 0.825 \text{ mg/mL})$$

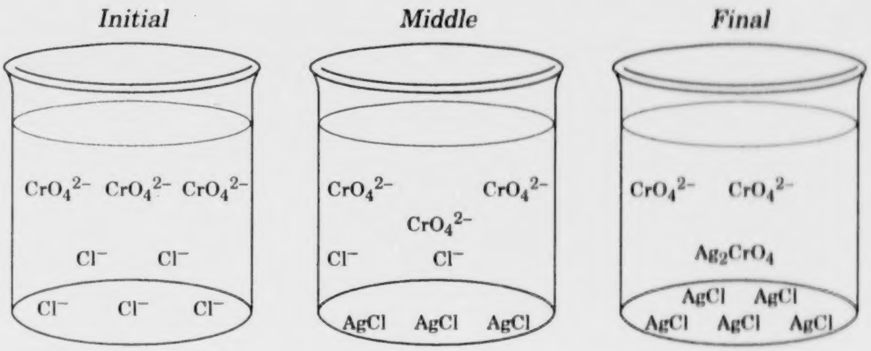
Pre-Laboratory Discussion

1. Discuss the dangers of too much salt in our diet. *[Hypertension, kidney disease, heart disease]*
2. Show Fritos® package, read list of ingredients and all nutritional information on label. Make overhead projection of label. Point out the amount of "sodium" on the label. Discuss with students: Is this metallic, elemental sodium or sodium in the form of a compound? *[Na ions.]* How can we determine the actual amount of NaCl present? *[By dissolving the salt in H_2O and analyzing for one of the ions.]*
3. Explain that these reactions are the basis of Mohr chloride analysis. It depends on the solubility of the two silver precipitates, AgCl and Ag_2CrO_4. If Ag^+ ion is added to a solution containing *both* Cl^- and CrO_4^{2-} ions, the AgCl will be precipitated first, because it is "less soluble in water" than the Ag_2CrO_4. The solubility concentrations are AgCl = 1.3×10^{-5} M, and $Ag_2CrO_4 = 1.3 \times 10^{-4}$ M. When all the chloride ion has been precipitated, the Ag_2CrO_4 starts to precipitate and the color changes from a creamy yellow to an orange almost like orange juice. This end-point is somewhat subjective, and students should keep all titration flasks for comparison until they finish at least three trials.
4. Show the reactions below. AgCl(s) is white; $Ag_2CrO_4(s)$ is red.

$$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

$$K_2CrO_4(aq) + 2AgNO_3(aq) \rightarrow Ag_2CrO_4(s) + 2K^+(aq) + 2NO_3^-(aq)$$

   Use a beaker or flask to illustrate the above reactions. Take 10 mL 0.01 M NaCl solution; add 20 drops of K_2CrO_4 solution; note color. Then add the $AgNO_3$ solution, dropwise, with swirling. Point out the color changes to the orange color that signals the end-point of the titration.
5. Discuss the reason for using a blank. A blank is used to correct for any chloride ion that may be present in the water being used. It normally has a value of about 0.2-0.3 mL, and must be subtracted from the amount of $AgNO_3$ solution used in the analysis of the sample.
6. Make sure that students understand the proper use of burets, how to fill them, and read the volume. Stress that they must rinse the burets 4-5 times with distilled water when the laboratory is over.
7. Review the proper use of transfer pipets and demonstrate prior to student use.
8. The following "Pictures in the Mind" can be used to develop an understanding of the phenomena occurring during titration.



Teacher-Student Interaction

1. What is the purpose of the "blank" in the titration? *[The blank is necessary because some chloride may be present in the distilled or deionized water. The value normally is only 0.2-0.3 mL.]*
2. Why is the blank value subtracted from the total $AgNO_3$ solution used? *[The blank value is subtracted from the total $AgNO_3$ used in order to correct for any chloride ions present in the water used to make the filtrate.]*
3. What are possible explanations for the chloride ion being present in the blank? *[If deionized water is used, some chloride could be present from ion exchange; or glassware may not be completely rinsed.]*
4. As students titrate, ask them to notice the red Ag_2CrO_4 forming and then disappearing with swirling. Get them to explain the process. *[The Ag_2CrO_4 forms and then dissolves as the AgCl precipitates preferentially because of its lower solubility.]*
5. Suggest that students keep the blank flask to compare with subsequent trials. This reference will help them be consistent in judging the end-point. It is helpful to keep all titration flasks lined up for color comparison. This makes it easy for the student to see if too much $AgNO_3$ has been added.

Anticipated Student Results

Average mL $AgNO_3$ used for the blank: 0.3 mL

Average mL $AgNO_3$ used for the sample: 7.3 mL

Mass of Fritos® used: 20.0 g

Total volume of filtrate: 600.0 mL

Answers to Data Analysis and Concept Development

3. $$\frac{\text{(avg mL AgNO}_3\text{ used − blank)}}{\text{10 mL filtrate}} \times \frac{\text{0.825 mg NaCl}}{\text{1 mL AgNO}} = \frac{\text{5.77 mg NaCl}}{\text{10 mL filtrate}}$$

$$\frac{\text{5.77 mg NaCl}}{\text{10 mL filtrate}} \times \frac{\text{600.0 mL filtrate}}{\text{20.0 g Fritos®}} = \frac{\text{17.3 mg NaCl}}{\text{1 g Fritos®}}$$

Answers to Implications and Applications

1. The National Research Council has defined an "adequate and safe" level of sodium as between 1000 and 3300 mg daily. Some physicians feel that this is too high and should be much lower, around 220 mg per day.
2. Answers will vary (see *Assessing Laboratory Learning,* Question 2, for a sample calculation).
3. Monitor the amount of salt in the diet.

Post-Laboratory Discussion

1. Make sure that students have calculated their analytical data correctly and averaged their results. Put class values on the board for comparison and discussion.
2. Assist students in calculating mg NaCl in the entire Fritos® package. Food values are given as "mg sodium," not "mg sodium chloride." Show students how to convert mg NaCl to mg Na.

$$\text{By ratio:} \quad \frac{\text{molar mass NaCl}}{\text{molar mass Na}} = \frac{\text{mg NaCl}}{\text{mg Na}}$$

$$\text{Unit Analysis:} \quad \text{mg Na} \times \frac{\text{molar mass NaCl}}{\text{molar mass Na}} = \text{mg NaCl}$$

3. Discuss discrepancies between the stated value and the experimental results.
4. Ask teams of students to make an estimation of one person's daily intake of sodium, using information from library sources such as *Composition of Foods* (U.S. Department of Agriculture, 1979).

Extensions

1. The Mohr Chloride analysis can be used for pretzels, potato chips, and other salty snack foods.
2. Analyze tap water, bottled spring water, and pond or stream water for chloride content.

Assessing Laboratory Learning

1. When a sample of pretzels was analyzed by the Mohr chloride method, the following data was obtained:

   Average mL for blank: 0.2 mL

   Average mL for sample: 13.5 mL

   Mass of pretzels used: 10.0 g

   Total filtrate volume: 300.0 mL

   Calculate the mg NaCl and the mg Na in a 1 ounce (28.4 g) serving of these pretzels.

$$\frac{13.5\text{ mL} - 0.2\text{ mL}}{10\text{ mL filtrate}} \times \frac{0.825\text{ mg NaCl}}{1\text{ mL AgNO}_3} = \frac{11.0\text{ mg NaCl}}{10\text{ mL filtrate}}$$

$$\frac{11.0\text{ mg NaCl}}{10\text{ mL filtrate}} \times \frac{300.0\text{ mL filtrate}}{10.0\text{ g pretzels}} = \frac{33.0\text{ mg NaCl}}{1\text{ g pretzels}}$$

$$\frac{33.0\text{ mg NaCl}}{1\text{ g pretzels}} \times 28.4\text{ g pretzels} = 937\text{ mg NaCl}$$

$$937\text{ mg NaCl} \times \frac{23.0\text{ mg Na}}{58.5\text{ mg NaCl}} = 368\text{ mg Na}$$

2. The following information was given on a snack label:

Package weight:	10 oz (283 g)
Serving size:	1/2 oz
Sodium per serving:	90 mg

   a. Calculate the mg NaCl per serving.

$$\frac{90\text{ mg Na}}{\text{serving}} \times \frac{58\text{ mg NaCl}}{23\text{ mg Na}} = \frac{227\text{ mg Na}}{\text{serving}}$$

   b. Calculate the grams of NaCl and teaspoons of NaCl in the entire package (1 teaspoon NaCl = 6 g).

$$\frac{0.227\text{ g NaCl}}{0.50\text{ oz}} \times \frac{10\text{ oz}}{\text{package}} = \frac{4.54\text{ g NaCl}}{\text{package}}$$

$$\frac{4.54\text{ g NaCl}}{\text{package}} \times \frac{1\text{ tsp NaCl}}{6.0\text{ g NaCl}} = 0.76\text{ tsp NaCl}$$

3. Obtain information from labels on products in the grocery store concerning the sodium content of the following: cookies, hot cereals, soda crackers, canned vegetables, dry cereals, canned fruit, popcorn, cheese-flavored snacks.

   Which of these foods would be recommended for a low-sodium diet? Compare the salt content of normal prepared spaghetti sauce with the low sodium variety.

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: Chromatographic Comparison of M&M™ Candies with Reese's Pieces™

Introduction

Colors in candies are due to synthetic dyes that have been approved by the Food and Drug Administration (FDA). Sometimes the colors such as greens and browns are mixtures of several dyes. In this laboratory we will separate the colors in M&M™ candies and Reese's Pieces™ by means of paper chromatography. Differences in the solubilities of the dyes will enable us to make the separation. The more soluble dyes will travel up the paper faster than dyes that are less soluble.

Purpose

To determine if the brown coloring matter in M&M™ candies is the same as the brown coloring matter in Reese's Pieces™. At the same time, other candy colors will be chromatographed to determine their component colors.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Do not eat any of the candy used in the laboratory activity.

Procedure

1. Obtain 3-4 brown M&M™ candies (or whatever color your teacher assigns). Place them in a small evaporating dish and place a few drops of tap water on them. Stir around with a toothpick to dissolve the color. As soon as the colored layer is dissolved, remove the piece from the dish with forceps and discard them.
2. Repeat with some brown Reese's Pieces™ in a second evaporating dish. Use clean toothpicks for each dish.
3. Obtain a piece of chromatography paper that will accommodate spots of both candy colors. Draw a light *pencil* line about 3 cm from the bottom edge of the paper and initial the paper in one upper corner. Put two pencil dots on the original pencil line, about 3 cm apart. Label one M&M™ and one Reese's Pieces™.
4. Using small capillary tubes place spots of each color on the labeled dot. The spots should be about 1 cm in diameter, and must not overlap. Let dry and apply more sample, keeping the spots as small as possible. Repeat until you have placed about 5-6 spots on each dot to make a concentrated sample.
5. Obtain the proper container for the chromatography (beaker or jar) and pour in salt solution until it is about 1 cm deep. Suspend the paper in the container as your instructor directs (see *Forensic Chemistry* module, Activity 1). Be sure that the lower end of the paper is just touching the solution, and that the solution does not reach the colored spots.
6. When the solution rises to within 3 cm of the top of the paper, remove the paper from the solution and allow to dry. Mark the position of the solution on the paper with a light pencil line.
7. Compare the chromatograms for each dye to determine if the candies contain the same dyes.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

Notice the number and colors of the spots on the two chromatograms. Draw circles around the spots that are common to the two candies. The spots must be the same color and must have traveled the same distance up the paper.

1. Is a pure brown dye used to color the candies?
2. If you wished to produce a green dye, what colors would you use?
3. Suppose you were given an unmarked bag of one of these candies. How could you distinguish chemically whether the contents were M&M's™ or Reese's Pieces™?

Implications and Applications

1. How could chromatography be used to distinguish some look-alike candies?
2. How could you tell which dyes were present in the candies?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: Chromatographic Comparison of M&M™ Candies with Reese's Pieces™

Major Chemical Concept

Paper chromatography can be used to separate the food colors in candy such as M&M™ candies and Reese's Pieces™, and can show the differences between the brown colors in the two brands.

Level

This activity is appropriate for all levels of chemistry classes.

Expected Student Background

None

Time

50-55 min. The activity can be broken into two 30-min time periods by doing Steps 1-4 on the first day and storing the prepared samples for later use.

Safety

Read the *Safety Considerations* in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

- 12 Chromatography jars with lids or stoppers (empty 12-16 oz jelly or spaghetti sauce jars)
- 12 Forceps
- 12 Lead pencils
- 12 Ringstands and buret clamps

Consumables

- 36-48 Pieces of each color and kind of candy
- 12 Chromatography paper (or filter paper) pieces cut to fit containers to be used (*e.g.*, 4 cm x 8 cm)
- 24 Capillary tubes
- Water, distilled
- 0.1% NaCl solution (dissolve 0.5 g NaCl in about 500 mL water)

Advance Preparation

Obtain the necessary amount of candy. Cut chromatography paper to fit containers. Prepare suspension apparatus for chromatography jars or tubes. A paper clip hook inserted in a cork is ideal for large test-tubes (see *Forensic Chemistry* module for diagram). Have a sample setup ready for students to use as a model.

Pre-Laboratory Discussion

Show an example of a chromatographic separation (such as the ink from a washable black marker or pen), and explain how paper chromatography can separate the colors. For use in foods, there are only 5 or 6 artificial colors that are approved by the Food and Drug Administration (FDA). A mixture of colors is required to give a brown color. Show students the candy and ask them if they think that the brown colors in each brand are made of the same mixture of colors. Paper chromatography will provide the answer.

Teacher-Student Interaction

Circulate in the laboratory. Check spots on prepared chromatograms to make sure they are properly placed and not too large.

Anticipated Student Results

The brown color is a mixture of red and blue dyes.

Answers to Data Analysis and Concept Development

1. No, blue and red.
2. Yellow and blue.
3. Carry out a chromatographic analysis using the M&M™ candies and Reese's Pieces™ along with the unknown. Check the chromatogram for a match.

Answers to Implications and Applications

1. Use paper chromatography to separate and compare the dyes used in the candies. Make sure that students are aware that there are only five or six food colors approved by the Food and Drug Administration (FDA), so some look-alike candies may indeed have chromatograms that look alike as well.
2. Obtain food dye samples of known composition to use as standards. A convenient source is the food colors sold in supermarkets since each color is labeled with the dye or dyes that it contains. Chromatographing these dyes side by side with the candy samples will probably help identify the candy dyes.

Post-Laboratory Discussion

Discuss this laboratory activity in terms of separation (see *Separations* module). Ask students why they think separations are so important to chemists. Ask students to suggest ways in which separations can be used in the food industry. Ask them to imagine that they are trying to break into a candy market that has been dominated by a certain manufacturer. What chemical information might they need? How can they obtain this information? How can the concept of chromatographic separations help? Explain that there are numerous commercial analytical laboratories that perform some of these functions for businesses. Also pertinent to this laboratory activity is the fact that Red (Dye) No. 3, used in fruit cocktail cherries, is being phased out by the FDA because extensive tests showed that this dye could cause thyroid cancer in rats. Ask students to discuss a way for testing for Red No. 3 in various food products. What products might they choose? Do these products necessarily have to be red? (See *Extensions.*)

Extensions

1. Students may wish to examine products at home or in the grocery store to find out which ones contain Red No. 3. Boxes of food colors state that they contain Yellow No. 5, Red No. 40, Red No. 3, and Blue No. 1. Students can use paper chromatography to determine the ingredients of green, red, and yellow colors. There are many other foods that can be chromatographed, such as numerous varieties of candy, diet Jello™, or Kool-Aid™. Washable colored pens are advertised as using only FDA approved colors, but do they? Design an experiment to verify or disprove these claims.
2. Do Activity 1 in the *Forensic Chemistry* module on identifying over-the-counter drugs by chromatography.

References

Red No. 3 and other colorful controversies. (1990, May). *FDA Consumer, 24*(4).

Additives for eye appeal. (1973, July-August). *FDA Consumer*.

Assessing Laboratory Learning

1. Draw representative chromatograms. Show how an unknown can be identified from a chromatogram.
2. Give students two chromatograms and have them identify the substance(s) common to both.

LABORATORY ACTIVITY: STUDENT VERSION

Activity 3: Analysis of Milk

Introduction

Milk is the complete food. It contains all of the major food groups required to meet the body's needs. You will analyze milk to determine the relative amounts of water and the three food groups—fats, proteins, and carbohydrates—contained in a typical milk sample.

Purpose

To determine the composition of milk.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. The extraction solvent fumes are volatile and harmful. Use under a fume hood or in a well-ventilated room.
3. Do not use mouth suction when filling pipets. Always use a pipet bulb. Your teacher will instruct you in its use.
4. When heating liquids, add boiling chips to avoid "bumping."
5. Dispose of excess liquids and solids as directed by your teacher.
6. Carefully read the laboratory activity before coming to the laboratory. Think about what you are going to do and plan ahead.

Procedure

Day 1

Part 1: Extracting and Determining the Percentage of Milk Fat in Milk

1. Weigh an empty 250-mL Erlenmeyer flask to ±1 g. Record mass in data table.
2. Using a graduated cylinder, add 100 mL milk to the flask and weigh again. Record mass in data table.
3. Using a second 100-mL graduated cylinder, add 100-mL nonpolar solvent (to be specified by your teacher) to the milk sample. Stopper the flask tightly.
4. Mix the flask contents for about 1 min by gently but repeatedly turning the flask over. Avoid vigorous shaking to prevent formation of small fat globules. The small globules increase the fatty material's surface area and trap nonfat materials in the fatty layer.
5. After mixing, allow the mixture to settle until the two layers are separated. The top layer is the nonpolar solvent layer; it contains the fat-soluble components of milk. The bottom layer is the aqueous layer; it contains the water-soluble components of milk.
6. Weigh a 250-mL beaker to ±1 g and record its mass in the data table.
7. Using a pipet, remove the aqueous (bottom) layer by successively withdrawing the liquid and transferring it into the weighed 250-mL beaker. The last portion can be withdrawn by having your partner tip the flask about 45 degrees to concentrate the remaining volume of water-soluble layer in the bottom of the flask and then carefully withdrawing as much as you can without mixing it with the nonpolar solvent layer.

8. Weigh the 250-mL beaker containing the aqueous layer and record the mass.
9. Using these data, calculate the percent milk fat in the original milk sample. Save bottom layer for use in Part 2; discard waste materials as directed by your teacher.

Part 2: Removal of Milk Protein

1. Add approximately 100 mL vinegar to the aqueous layer from Part 1, Step 8. Stir the sample slowly until solid clumps appear in the liquid.
2. Weigh a piece of filter paper and record mass in your data table.
3. Place the filter paper in a Buchner funnel fitted to a suction flask, wet it with a little distilled water and suction filter the coagulated material in the beaker. Continue to apply suction for about 5 min after all the liquid has passed into the suction flask; this strategy will help in drying your coagulated sample.
4. Carefully remove the filter paper and contents from the Buchner funnel and place on a watch glass that has been previously marked with your initials. Allow the filtered material, which consists largely of milk protein, to dry overnight.
5. Dispose of the liquid in the suction flask as directed by your teacher.
6. Thoroughly wash your hands before leaving the laboratory.

Day 2

Part 3: Determination of Percentage of Milk Protein

1. Weigh filtered, dried milk protein plus filter paper and record mass in data table.
2. Calculate the percent protein in the original milk sample.

Part 4: Determination of Percentages of Water and Carbohydrates in Milk

1. Weigh a small evaporating dish (the size should be large enough to be seated on top of a 250-mL beaker) and stirring rod together to ±0.1 g. Record mass in data table.
2. Using a 10-mL graduated cylinder, add 5 mL fresh milk to the evaporating dish and weigh again. Record mass in data table.
3. Set up a ringstand, ring, wire gauze and burner. Half fill a 250-mL beaker with water, add a few boiling chips, and place on the assembly.
4. Place the evaporating dish and contents on top of the 250-mL beaker from Step 3. Heat the water in the beaker to slowly evaporate the liquid from the milk sample. As a thin layer of scum forms on the milk, break it up with the stirring rod, making sure that you keep the stirring rod inside the dish. Stir the milk gently and continuously to avoid scorching.
5. As the milk dries, it becomes pasty. When the paste consistency appears to remain constant for a few minutes, stop heating. Allow the dish to cool. Wipe the condensed water from the outside of the dish. The dish now contains the milk solids.
6. Weigh the dish, stirring rod and milk solids, and record mass in your data table.
7. From these data, calculate the percent water in the original milk sample.

8. Knowing the percentages of fat, protein, and water contained in milk, calculate the percent carbohydrate by difference. Assume that the major components of milk are fat, protein, water, and carbohydrates only.
9. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

Data Table

Part 1

Mass of flask + 100 mL milk	(g)
Mass of flask	(g)
Mass of 100 mL milk	(g) [A]
Mass of 250-mL beaker + aq. layer	(g)
Mass of beaker	(g)
Mass of aqueous layer	(g) [B]
Mass of fat extracted [A - B]	(g) [C]

Parts 2 and 3

Mass filter paper + milk protein	(g)
Mass filter paper	(g)
Mass milk protein	(g) [D]

Part 4

Mass evaporating dish, stirring rod, and milk before heating	(g) [F]
Mass evaporating dish, stirring rod	(g) [E]
Mass of milk [F - E]	(g) [G]
Mass evaporating dish, stirring rod, and milk solids after heating	(g) [H]
Mass of milk solids [H - E]	(g) [J]
Mass of water evaporated [G - J]	(g) [K]

1. From your data, calculate:

	Laboratory value	Average accepted value
Percent milk fat (C/A) x 100	%	3.3%
Percent milk protein (D/A) x 100	%	3.3%
Percent water in milk (K/G) x 100	%	88%
Percent milk carbohydrate	%	4.5%

2. Compare your milk analysis with actual amounts listed on a carton of milk.
    a. Can you account for any difference between your results and the listed values?
    b. Why do you think that these average values do not total 100%?
    c. Explain why your laboratory values total 100%.
3. In Part 1, Step 3, why did you use a nonpolar solvent to extract milk fat?
4. In Part 1, Step 4, what effect would trapping of nonfat milk content in the fat-soluble layer have on your results?
5. In Part 1, Step 7, what effect would extracting some of the top layer along with the bottom layer have on your results?
6. In Part 2, Step 1, why does vinegar coagulate the protein?
7. In Part 4, Step 1, why did you weigh the stirring rod along with the evaporating dish?
8. In Part 4, Step 4, why did you heat the milk over water? What effect would losing some of the milk solid have on your results?

Implications and Applications

1. Powdered milk is primarily composed of the milk proteins and carbohydrates. Calculate the percent composition of powdered milk from the previous data. Would powdered milk be a good high protein supplement to add to other foods?
2. Have you ever accidentally poured orange juice into milk at breakfast? What happened? Why?
3. In the introduction, milk was discussed as a complete food. Can you name the principal proteins and carbohydrates in milk?
4. We have studied whole milk. There are other types of milk like 2% milk, 1% milk, and skim milk. What do these names imply about the milk composition?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 3: Analysis of Milk

Major Chemical Concept

The methods for extraction of milk components are based upon their chemical differences:

Fats: Extraction from a polar emulsion with a nonpolar solvent.
Proteins: Precipitation by denaturation.
Water: Evaporation.
Carbohydrates: By difference.

Level

For all levels of high school chemistry.

Expected Student Background

Students should be familiar with the properties of fats, proteins, and carbohydrates.

Time

Two 50-min periods. It is not necessary for the laboratory periods to be on consecutive days.

Safety

1. Read the *Safety Considerations* in the *Student Version*.
2. The nonpolar solvent is volatile and has hazardous fumes.

Materials (For 24 students working in pairs)

Part 1

Nonconsumables

Balances
24 Graduated cylinders, 100-mL
12 Erlenmeyer flasks, 250-mL
12 Stoppers to fit flasks
12 Transfer pipets and bulbs (size appropriate for extracting in steps 100 mL aqueous layer from milk sample); alternatively, separatory funnels
12 Beakers, 250-mL

Consumables

Fresh Whole Milk, 1.2 L
Nonpolar solvent, 1.2 L (see *Advanced Preparation*, Part 1)

Parts 2 and 3

Nonconsumables

12 Buchner funnels, suction flasks; alternatively, funnels, *fluted* filter paper
12 Spatulas
12 Beakers, 250-mL
12 Watch glasses

Consumables

Aqueous layer (from *Part 1*) in 250-mL beaker
Vinegar, 1.2 L
12 Filter papers (to fit Buchner funnel)

Part 4

Nonconsumables

12 Graduated cylinders, 10-mL
12 Evaporating dishes
12 Glass stirring rods
12 Beakers, 250-mL
12 Ringstands
12 Ring clamps
12 Wire mesh
12 Burners

Consumables

Milk, 60 mL
Boiling chips

Advance Preparation

Part 1

1. Purchase fresh whole milk. (Lowfat milks do not work very well.) Check the label on the carton to see if the declared values match those given to students in the data table. Adjust accordingly.
2. Use separatory funnels if they are available instead of the pipets in Part 1, Step 7.
3. Possible nonpolar solvents include trichlorotrifluoroethane (TTE), hexane, cyclohexane, and dichloromethane. Consider the hazards and cost for using each solvent. *NOTE: TTE is available as DuPont TF Solvent from dry-cleaning supply companies; this technical grade solvent is considerably less expensive than higher-grade TTE found in some chemical supply catalogs. Mix equal amounts (1 mL) of each nonpolar solvent and water to determine position of water layer.*

Part 2 and 3

1. A Buchner funnel and aspirator is ideal for the filtration of the protein. If not available, filter material through *fluted* filter paper to hasten filtration.
2. If filter paper is used, remember to remove the filter paper containing the protein from all students' funnels for overnight drying at the close of the first day. Set them on paper towels to dry overnight. Try not to leave the protein sample in one large clump (low surface area retards drying). Spread the protein thinly on the filter paper with a spatula. Leave the appropriate beaker and filtrate next to each filter paper.
3. Air drying will not remove all the water from the protein. However, the mass of the water remaining is not large enough to affect the students' results in any significant way. If desired, the protein could be given a final wash with ethanol to hasten drying.
4. Only the casein fraction of the protein is removed during protein extraction. The whey proteins (β-lactoglobulin and α-lactalbumin) are not precipitated. Thus it is incorrect to claim that this procedure measures "all" milk protein. However, since casein is the major protein in milk, student results will be quite acceptable.

Part 4

1. The stated procedure in Part 4 is not a very effective way to remove the moisture from the milk sample, but it has been bench tested and has produced good results. However, you can consider using a small convection oven if one is available.

Pre-Laboratory Discussion

Discuss solvent extraction, polar and nonpolar solvents, two layers and how to know which is which. Discuss precipitate formation, evaporation of a liquid and the effects of heat on the rate of evaporation.

Teacher-Student Interaction

Circulate in the laboratory. Demonstrate use of pipet bulb. Buchner funnels will be new to students; show them how to remove filter paper from the funnel.

Anticipated Student Results

1. Laboratory values to be expected:

Percent milk fat	2.7 - 4.1%
Percent milk protein	2.8 - 4.0%
Percent water	85 - 92%
Percent carbohydrate	3.5 - 5.5%

2. a. The reported values are averages. Each sample of milk will vary from the average values. Experimental error can account for some of the differences: balance accuracy and precision, extraction errors, *etc.*

   b. The average values do not total 100% because of the uncertainties in the reported values and the presence of small quantities of other components, such as vitamins and minerals.

   c. Student values total 100% because the carbohydrate value was obtained by subtracting the total of the other measurements from 100. The assumption was made that the contribution of the other components in milk was negligible and that the carbohydrate percentage could be determined indirectly by difference.

3. Fats are nonpolar and dissolve more readily in nonpolar solvents.

4. The extraction of nonfat milk components would be incomplete and yield high results for the percentage of milk fat.

5. Some of the fat-soluble layer would be weighed with the bottom layer and give low results for the percentage of milk fat.

6. Acids cause denaturation of proteins (see *Enzymes* module). Proteins lose their three-dimensional configuration that allows them to be water-soluble, and they precipitate out of solution.

7. The milk solid residue will collect on the stirring rod while stirring the mixture. Since it would be impossible to remove all of the solids from the rod in order to weigh the residue, the weight of the rod is counted from the beginning to minimize the error from this experimental step.

8. The milk would char or burn if subjected to extreme temperatures such as the direct flame of a burner. Losing some of the milk solid would cause a higher percentage of water to be reported.

Answers to Implications and Applications

1. 3.3 g (protein)/7.8 g (total protein + carbohydrate) = 42% protein. Powdered milk qualifies as a high protein supplement due to the large amount of protein per unit mass.
2. Milk proteins curdle in acid. Orange juice is acidic and can curdle (aggregate) protein.
3. Casein (protein) and lactose (carbohydrate).
4. The percent composition of fat in the milk.

Post-Laboratory Discussion

Look at the different types of milk and show the different contents. Some examples are 2%, skim, evaporated, powdered, baby formula, goat milk, and deer milk. Discuss the advantages and disadvantages of each type of milk.

Extensions

1. Extend this concept to the energy and nutritional value of milk. Calculate the calories in milk using the results of the activity (protein or carbohydrate = 4 cal/g; fat = 9 cal/g). Look at the minerals and vitamins in milk and check if they have been added as part of the fortification of milk.
2. Bromine is decolorized by unsaturated fats. Have students do library research on the degree of unsaturation of fats in milk and report on it in the context of other fatty foods.

Assessing Laboratory Learning

1. Ask students to explain why the mineral and vitamin content is considered insignificant in the determination of milk composition.
2. Ask students to list several common substances that they would expect to coagulate milk, and to explain why.
3. Ask students why we extracted and weighed the aqueous layer if they were determining fat content, which was contained in the fat-soluble layer.

DEMONSTRATIONS

CAUTION: Use appropriate safety guidelines in performing demonstrations.

Demonstration 1: "Light" Margarine, Paying More for Less

Purpose

To demonstrate the amount of water in regular, light, and "extra light" margarines.

Materials

Three kinds of margarine from one manufacturer (*i.e.*, Regular, Light, and Extra Light Fleischmann's margarine)
3 Graduated cylinders, 10-mL (glass, heat-resistant)
3 Beakers, 100- or 250-mL (glass, heat-resistant)
3 Stirring rods
Balance
Hot plate or burner

Procedure

Prepare ahead of time:

1. Melt 10 g of each margarine in separate beakers. Heat gently, stir constantly; do not allow to boil.
2. While stirring continuously, pour each sample of melted margarine into a labeled 10-mL graduated cylinder, filling exactly to the 10.0-mL mark. Allow to cool. Keep covered and refrigerated until ready to perform the demonstration.
3. Photocopy (or type) the nutritional labels from each kind of margarine and make overhead projections (OHPs) and/or copies for the students.

The demonstration:

1. Show the margarine packages. Show the OHPs and/or hand-outs and point out that the amount of fat *is* decreasing (just as the ads say), along with the calories, as one compares the different margarines: Regular → Light → Extra Light.
2. What is the *first* ingredient listed in each label? *[In Regular and Light, it is "liquid corn oil," but in Extra Light, it is water.]*
3. Show the students the prepared graduated cylinders, with the layer of water on the bottom of each. A light box or diffused light source behind the tubes will make the layers clearly visible. (One could also make a drawing on the OHP, showing the amount of water in each product.)
4. List the percent water found by examining the graduated cylinders:

Regular	3%
Light	20%
Extra Light	35%

(*NOTE: There is a white layer between the water and the oil layers; this is probably the whey that is listed in each ingredient list.*)

5. Discussion (the discussion of Topics f and g could lead to several student projects):
    - a. Reasons why consumers buy Light and Extra Light.
    - b. How many of the students use these products at home.
    - c. What is the cost/pound for each type? (Recent purchase of Fleischmann's Regular = $1.29; Light = $1.39; Extra Light = $1.79)
    - d. Why do Light and Extra Light cost more, even though they contain less fat and more water?
    - What is the cost/pound of the actual fat in each margarine?
    - f. What two types of fats are listed on the label? Why do they *not* add up to the total amount of fat in the margarine? What other kind of fat is present?
    - g. Saturated *vs.* unsaturated fat controversy: What is the effect of dietary saturated fat on blood cholesterol levels?

Extensions

Have the students bring in samples of other margarines, butter, "soft butter," and butter "taste-alikes" to test for water content.

Demonstration 2: Extraction of Iron from Cereal: The Oxidation States of Iron

Purpose

To extract iron from cereal and determine its oxidation state. Elemental iron in the form of minute iron filings can be extracted from cereal with a magnet. To dissolve the extracted iron in simulated stomach acid and determine its oxidation state. When dissolved in 0.1 M HCl, both the Fe(II) and Fe(III) oxidation states are obtained.

Materials

Nabisco Instant Cream of Wheat (individual serving packets work best)
Beakers
Test-tubes
Magnetic stir bar and stirrer
0.1 M HCl [simulated stomach acid; 4 mL conc. HCl (12 M) to 500 mL solution]
0.1 M KSCN Potassium thiocyanate [Add 0.97 g KSCN to water and dilute to 100 mL]
0.1 M $K_4Fe(CN)_6$ Potassium ferrocyanide [Add 3.7 g $K_4Fe(CN)_6$ to water and dilute to 100 mL]
0.1 M $K_3Fe(CN)_6$ Potassium ferricyanide [Add 3.3 g $K_3Fe(CN)_6$ to water and dilute to 100 mL]
0.1 M Fe(II) Salt such as $FeSO_4$ or $Fe(NH_4)_2(SO_4)_2$ [Add 0.01 mole of either to water and dilute to 100 mL]
0.1 M Fe(III) Salt such as $FeCl_3$ or $Fe[NO_3)_3$ (Add 0.01 mole of either to water and dilute to 100 mL]

Safety

Use normal safety precautions.

Procedure

Show boxes of cereals and note the ingredient listing for iron. This listing could read "iron," "elemental iron," "reduced iron," or some iron compound [usually Fe(II)]. "Reduced iron" is elemental iron. Explain to students that in order for iron to be absorbed in the intestines, it must be in the Fe(II) state. Ask them how we could get the iron out of the cereal. What forms of iron could be removed with a magnet?

Extract the iron by crushing and stirring the dry cereal with the stir bar for about 5-10 min. Extract the stir bar from the cereal. Let students examine it. They will note the iron "whiskers" clinging to the bar. Place the stir bar in a beaker with 100 mL 0.1 M HCl. Explain that the sample has to stand several days in order for the iron to dissolve. Compare the pH of the HCl to that of the stomach. Compare the conditions of the demonstration with that of iron in the stomach, *e.g.*, temperature, agitation, and time in the HCl solution. The stomach empties about every 2-3 hr.

Cover the beaker and examine it every day for a week. Point out that the iron has dissolved. Ask what compound is present. Students will say iron chloride. But which one?

In test-tubes, show the reactions of known iron salts with the reagents, making a table as shown. Using these results, determine the oxidation state of iron dissolved in the acid.

	KSCN	$K_4Fe(CN)_6$	$K_3Fe(CN)_6$
Fe^{2+} solution	—	Milky blue	Dark Blue
Fe^{3+} solution	Red	Dark blue	Clear green
Dissolved iron solution	Red	Dark blue	Dark blue

Remarks

The following questions might be used in discussing the demonstration:

1. What is the oxidation number of Fe in $K_4Fe(CN)_6$? *[+2]* In $K_3Fe(CN)_6$? *[+3]*
2. Write balanced equations for each color of solution or precipitate formed in the tests.

   $Fe^{2+} + SCN^- \rightarrow$ No reaction

   $Fe^{3+} + SCN^- \rightarrow [FeSCN]^{2+}$ (red)

   $Fe^{2+} + Fe(CN)_6{}^{3-} \rightarrow Fe_4[Fe(CN)_6]_3$ (dark blue)

   $Fe^{3+} + Fe(CN)_6{}^{4-} \rightarrow Fe_4[Fe(CN)_6]_3$ (dark blue)

   $Fe^{2+} + Fe(CN)_6{}^{4-} \rightarrow Fe_2[Fe(CN)_6]$ (milky blue)

   $Fe^{3+} + Fe(CN)_6{}^{3-} \rightarrow Fe[Fe(CN)_6]$ (green)
3. From your observations, draw a conclusion about the oxidation number of the iron dissolved in the HCl. Write formula(s) and name(s) for the compound(s) formed. *[Both will be present: $FeCl_2$, iron(II) chloride, and $FeCl_3$, iron(III) chloride.]*
4. If iron dissolved in the stomach as slowly as it did in the beaker, would the iron in your breakfast cereal be beneficial to you? *[No, it would not be in an absorbable form.]*
5. Of what use is iron in the body? *[It is part of the heme molecule, which carries oxygen in the blood. The oxidation state of iron in the heme is +2.]*

Extensions

Read other labels on vitamins, *etc.* to determine the form of iron present. Iron is seldom eliminated from the body. Unless you have a disease such as anemia or lose blood, you probably do not need extra iron; however, pregnant and postpartum women may need supplements.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. Does food consist of chemicals? *[Yes.]*
2. How can a knowledge of chemistry help you decide what food to eat or buy? *[You can read and interpret the labels and not be fooled by false or ambiguous advertising.]*
3. An advertisement states that a prune, ounce for ounce, has more vitamins than a plum. Why is this statement misleading? *[Only water is removed from the plum to make a prune. The vitamins remain, but the mass is less. You get the same mass of vitamins from a prune as from a plum.]*
4. Are food additives bad? *[Not always; they can protect from spoilage and deficiency-diseases.]*

Counterintuitive Examples

1. Labels do not tell the whole story. There are many prepared foods that contain compounds that cannot be digested; drugs or cosmetics may contain compounds to which one is allergic; drugs or foods may contain nutrients in a form the body does not use.
2. Enriched flour *vs.* whole wheat flour. White flour is prepared by removing some of the bran and germ. White flour is bleached with benzoyl peroxide. Enriched flour has had nutrients added to it. The whole wheat flour is made from the whole grain. It may also have added nutrients. It does not last as long as white flour because the oil from the wheat germ becomes rancid, so preservatives are often added.
3. Refined white sugar *vs.* honey. White sugar is recrystallized sucrose, a chemical combination of glucose and fructose, extracted from sugar cane or sugar beets, usually by concentrating the syrup and letting the crystals form. The brown decomposition products of this process are removed in the refining. Brown sugar is white sugar to which molasses has been added. When sucrose is eaten, an enzyme in the body changes it to glucose and fructose. Honey is a solution of sugars produced by bees, a 50/50 mixture of glucose and fructose. In terms of sugar content, refined white sugar and honey are equivalent. Judgments regarding the choice of honey over refined sugar become matters of personal preference.
4. All food additives are harmful. Preservatives, such as sugar and salt, and antioxidants, such as lemon juice, have been used for thousands of years as additives. Additives can be very important in an urban society where food may be shipped long distances before being used. The safety of the additives is monitored by the FDA. However, some people may have a reaction to a specific additive, such as MSG (monosodium glutamate) and should read labels or inform food providers of the problem.
5. It is safe to eat fat or food containing cholesterol. Some fat and cholesterol are necessary for healthy body functions. The body even manufactures cholesterol for its use and uses it for the vital biological role of the formation of steroid hormones (sex hormones) and Vitamin D. If the body does not provide enough cholesterol, some must be eaten. Fats are a source of long term energy storage.

Group Discussion

1. Compare expensive and inexpensive nutrients such as vitamins and Ca^{2+} supplements. Compare contents and quantity. What makes the difference in the price? Use the *Merck Index* or a *Physician's Desk Reference* to identify ingredients.
2. How does a microwave oven work? Why must you vent the food in a microwave oven? Microwaves are a form of electromagnetic energy, with a shorter wave length and higher frequency (more energy) than radio waves and longer wave length and shorter frequency than visible light. Microwaves are like radar emissions and are absorbed by water, but are reflected by metal; they pass through glass, paper, and plastic. When the energy is absorbed, primarily by the water in the food, the molecules begin to move rapidly and produce heat to cook the food. They do not cook "from the inside out," but if allowed to stand, the heat will be conducted inward, cooking as it travels. Because the steam produced from the liquid water in the food can become very hot when microwaved in a closed space, all food should be vented and care used before opening microwaved packages.

3. Read and interpret food labels. The ingredient present in the greatest concentration is first on the list. Answer the following questions:

SUPER BRAN FLAKES

Nutrition Information per Serving

Serving size:		1 oz (2/3 cup)
Servings per container:		15
	1 oz cereal	1 oz cereal plus 1/2 cup Vitamin D fortified whole milk
Calories	85	160
Protein	3 g	7 g
Carbohydrate	20 g	25 g
Fat	0 g	4 g
Sodium	280 mg	350 mg
Potassium	200 mg	360 mg
Percentage of U.S. Recommended Daily Allowances (U.S. RDA)		
Protein	5	19
Vitamin A	<2	5
Vitamin C	20	20
Thiamine	20	20
Riboflavin	5	12
Niacin	20	25
Calcium	<2	20
Iron	20	20
Vitamin D	<2	10
Vitamin B_6	20	20
Folic Acid	20	20
Vitamin B_{12}	20	24
Phosphorus	18	26
Magnesium	10	13
Zinc	20	25
Copper	8	8
Pantothenic Acid	2	6

Ingredients: Wheat bran, milled yellow corn, sugar, malted cereal syrup, salt, sodium ascorbate, niacinamide, reduced iron, zinc oxide, BHA, pyridoxine hydrochloride (Vitamin B_6), thiamine mononitrate (Vitamin B_1), folic acid, Vitamin B_{12}.

a. How many cups of cereal will this package provide? *[2 / 3 X 15 = 10 cups]*

b. How many calories are in one serving of the cereal? *[85 cal]*

c. How many calories are *added* when you eat the cereal with $^1/_2$ cup of whole milk? *[75 cal]*

d. Does a serving of cereal plus milk provide more grams of protein, fat, or carbohydrate? *[Carbohydrate]*

e. If you are 18 years old, you need 80% of the U.S. RDA for Vitamin C. How many servings of this cereal would you have to eat in order to meet your need for Vitamin C? *[One serving provides 20%; to get 80%, one needs four servings.]*

f. If you ate two cups of this cereal, what percent of the U.S. RDA for niacin would be supplied by the cereal alone? *[$^2/_3$ cup provides 20%, and to get 2 cups, you need to eat three servings; hence, 3 X 20% = 60%.]*

g. How much more niacin would be supplied by 2 cups of this cereal plus milk? *[$^2/_3$ cup with milk provides 25%, and 2 cups would supply 75%; hence, 15% more.]*

h. What ingredients are found in the smallest and largest amount? *[Vitamin B_{12} and wheat bran, respectively.]*

i. What minerals are provided by this cereal? *[Sodium, potassium, calcium, iron, phosphorus, magnesium, and copper]*

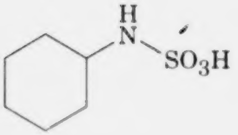
j. Which would provide less fat when used with this cereal: Vitamin D fortified or skim milk? *[Skim milk contains less fat than whole milk.]*

k. What is the function of the BHA? *[Food preservative]*

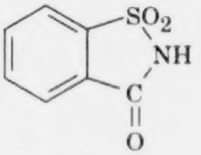
l. How is Vitamin C identified in the list of ingredients? *[Sodium ascorbate]*

4. Discuss artificial sweeteners: saccharin, cyclamate, NutraSweet™ (aspartame) and Sweet One™ (acesulfame K).

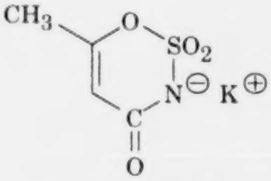
TABLE OF RELATIVE SWEETNESS	
Sweetener	**Relative Sweetness (mass for mass)**
Fructose	>1.0
Sucrose (cane sugar)	1.0
Cyclamate	30-80
Acesulfame K	150
Aspartame	100-200
Saccharin	500-700



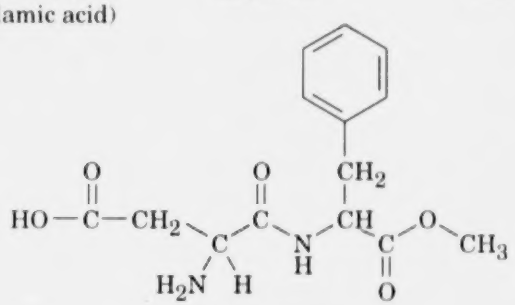
Cyclamate
(Cyclamic acid)



Saccharin



Acesulfame K



Aspartame

a. Which sweeteners are presently approved for use in the U.S.? *[All except cyclamate]*

b. Which one is most used in soft drinks? *[Aspartame]*

c. Which ones are destroyed by heat? *[Aspartame and saccharin]*

d. Which ones are not destroyed by heat? *[Acesulfame K and cyclamate]*

e. Which one is metabolized by the body? *[Aspartame]*

5. Discuss artificial fats, Simplesse, Olestra.

Current medical information linking heart disease to saturated fats has prompted chemical manufacturers to develop artificial fats. Both Procter and Gamble and the NutraSweet™ Company have developed fat substitutes.

Simplesse™, developed by chemists at NutraSweet™, is an all natural fat substitute made from milk protein. It contributes only 1-2 calories per gram versus 9 calories per gram for fat. Each Simplesse particle consists of several million loosely packed protein molecules. Their round shape and uniform size allows the particles to roll easily over one another, creating the smoothness and richness normally associated with fat. Simplesse has found uses in ice cream, yogurt, salad dressings, and sour cream. However, since it is a protein, it cannot be used in baked or fried foods.

Olestra™, developed by Procter and Gamble, is a fat replacement that can be used in frying, cooking, and baking, because it is made from fat. Conventional fats are esters of glycerol and three fatty acid chains. Olestra is composed of sucrose with 6 to 8 fatty acid chains, usually produced from soybean or corn oil. Because Olestra is a larger molecule than a fat molecule, it is not hydrolyzed by the body's digestive enzymes. Olestra will be used to substitute 35% of the fat in oils and shortenings used in the home and up to 75% of the fats used in restaurants for deep frying and in the commercial production of fried snack foods. Olestra may also, someday, be found in ice cream, yogurt, and salad dressings. Both companies will make literature on their products available to schools.

6. Discuss cholesterol and fats (saturated and unsaturated) and the relationships between these substances (see *Organic Chemistry* module).
7. Read labels on vitamins and determine whether prices reflect differences in content. Compare standard brands with generic brands and with those called "natural." Rose hips can be used as an example.
8. Using McDonald's publications, determine the contents of a fast food lunch (see *Appendix*).
9. Analyzing Foodstuffs for Food Additives (or Is That Stuff Really in My Food?)
10. **Student Activity**

    Students should collect food labels for one week prior to starting this activity. Teacher leads discussion on the 11 categories of food additives (see *Appendix*).

    a. Distribute the labels in plastic baskets among pairs of students.
    b. Each pair should look at the ingredient section on the labels and find two additives for each of the 11 categories on the chart (see *Appendix*).
    c. As each pair of students finishes looking through a basketful of labels, it is passed to an adjacent group, and they receive a different basket. This should take about 30 min.
    d. On the board, construct a table like the one in the student handout, and ask students to fill in with the additives they found.

Language of Chemistry

TIPS FOR THE TEACHER

carbohydrate polyhydroxy aldehyde or ketone with a hydrogen/oxygen ratio of 2:1; all natural carbohydrates are produced by plants except glycogen.

cholesterol steroid found in animal cells; building block of many steroidal compounds, including many hormones.

fat triacylglyceryl ester formed by mainly saturated long chain fatty acids with glycerol; melting points of fats are generally above room temperature.

fatty acid long chain carboxylic acid that may be saturated or have varying degrees of unsaturation.

glycerol triol with the formula $C_3H_8O_3$ that forms the "backbone" of fats and oils; since three fatty acid residues are bonded by ester linkages in fats and oils, these compounds are called triglycerides.

lipid group of fat-soluble compounds that includes fats, oils, waxes, phosphatides, cerebrosides, and terpenoids (of which steroids are a subclass).

minerals, dietary inorganic elements that play an essential role in certain body functions; some are present in fairly large quantities and some are present in trace amounts.

oil triacylglyceryl ester formed by mainly unsaturated long chain fatty acids with glycerol; melting points of oils are general below room temperature.

protein macromolecule composed principally of long chains of amino acids.

saturated term describing organic compounds with only carbon-carbon single bonds.

unsaturated term describing organic compounds with double and/or triple carbon-carbon bonds.

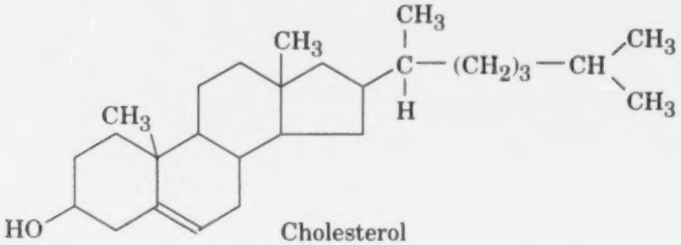
vitamin organic compound essential for the growth and survival of an organism but that the organism cannot synthesize for itself.

Common Student Misconceptions

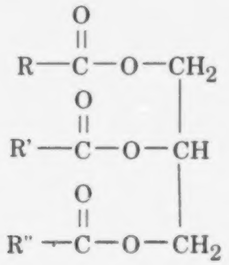
"Organic" foods are better than "processed" foods. Chemical compounds have the same formula wherever they are produced. Oyster shell calcium carbonate is the same as calcium carbonate precipitated in the laboratory.

Other

1. **Cereal and additives**. Check the labels for additions to your cereal. Check on the form of iron; "reduced iron" almost always means elemental iron; iron(III) salts precipitate in the intestine (pH = 10) as $Fe(OH)_3$; iron(II) salts are stabilized as complexes (heme iron).
2. **Orange juice with calcium**. Check on the form of calcium added. The acid in orange juice could dissolve any calcium carbonate, releasing CO_2, but other additives might not dissolve in the stomach acid. Is orange juice with added calcium a good buy? *[No; very expensive.]*
3. **New Horizons bread**. This bread is advertised as having fewer calories and more fiber. It contains cellulose, which is not metabolized and, therefore, provides fewer calories. Cellulose is also not useful as fiber in humans. Some "light" breadstuffs, such as frozen pancakes, also have a large amount of cellulose.
4. **Eggs and cholesterol**. Egg yolks, but not the whites, contain cholesterol. Egg substitutes are often made from the whites.
5. **Analysis of nutrition in hamburger and french fries**. Although there is still a debate over the disadvantage of saturated fats and their relationship to hardening of the arteries and cholesterol, students should be aware of these studies. Current research indicates that mono-unsaturated fats may be better than polyunsaturated or saturated fats. We know that cholesterol is carried in the body by high density lipoproteins to the liver to be excreted and by low density lipoproteins through the blood stream. This knowledge has led to the erroneous nomenclature, "good" cholesterol (HDL) and "bad" cholesterol (LDL). Cholesterol has a different chemical formula and is a different compound from lipoproteins and triglycerides.



Cholesterol



Triglyceride

R, R', R'' are fatty acid residues

(Lipoproteins are conjugates of lipid and protein)

See Transparency of McDonald food components and *ChemMatters* article (see *References,* Baugh, 1989).

6. **Sodas and yogurt**. Notice the caffeine in colas and the presence of phosphoric acid. Notice the low pH of these compounds. Sodas are substitutes for commercial acids in automobile garages, *etc.* Notice how the Calories in yogurt depend upon the kind of milk (% fat) used in its production.
7. **Food additives, nitrites, nitrates, ascorbic acid or sorbates, dyes**. There are several different types of food additives: (GRAS additives are "generally regarded as safe.").
   a. **Preservatives**. To prevent spoilage and keep food fresh.
   b. **Antioxidants**. To keep fats from getting rancid.
   c. **Coloring matter**. To improve appearance (see *References,* McKone, 1990).
   d. **Flavoring agents**. Compounds, both natural and synthetic, to flavor and artificial sweeteners.
   e. **Sweeteners**
   f. **Sequestrants**. To tie up metal ions that can cause decomposition of foods
   g. **Gelling agents, stabilizers, and emulsifiers**. To give foods a desired consistency.
   h. **Acids and bases**. To increase tartness or lower pH (*e.g.*, to inhibit crystallization) for acids. Bases are used in baking powder or to provide CO_2.
8. Many foods such as peanuts, margarine, *etc.* carry a "no cholesterol" label. Are these foods more healthy than unlabeled "generic" peanuts and margarine? No. Only animal products contain cholesterol. Unless animal products have been added to foods like peanuts and margarine, any brand chosen will be cholesterol-free.

HISTORY: ON THE HUMAN SIDE

The Ethylene Glycol Tragedy that Triggered the Formation of the FDA

In the 1930's there were no laws in the United States that required drug manufacturers to test drugs before selling them to the public. However, in 1937, 107 people (mostly children) died after taking a liquid formulation of sulfanilamide. "Sulfa" was the first of the"wonder drugs," and a drug company had discovered that it dissolved well in ethylene glycol. Ethylene glycol, ordinarily used for antifreeze, has an appealing sweet taste, but it is extremely toxic. The public outrage was so great that Congress passed the 1938 Food, Drug and Cosmetic Act, which required that drugs be cleared for safety *before* they are put on sale in the marketplace.The young researcher, who discovered that it was ethylene glycol that killed the victims, was the same person, who in the 1960's, stopped thalidomide from being sold in the United States, Dr. Frances Kelsey.

HUMOR: ON THE FUN SIDE

1. **A chemical code**:

   For "AsO_4^{3-} $C_6H_{12}O_6$" read, "Our son ate glucose."

   CHEM 13 NEWS, September 1979, p. 11

2. Word Search (see *Appendix* for master copy)

A D C A M X N A C E E X O E O Q C
F F G Z ~~F A T S~~ F T D U Y I Z A N
R L L A R U R P U F I N P L R M T
I O ~~M U I C L A C~~ X R U V B W M U
K R K S Z F W R P F E S O G T O V
M E C J D S J T E Q C H O K W L W
Y T N N L W P A D T Y P E C Q A I
T S X I N Z R M F D L M J M Z S B
T E Q F M J N E R U G W H L E S M
A L D U M A R A A S I F M O V E H
L O T K R U T K I W R I B P J S N
O H D A U E S I K V T P G X W V O
T C Z U F G A B V B ~~N I E T O R P~~

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Polyhydroxy aldehyde or ketone.
2. Peptide with more than 100 amino acid residues.
3. Lipids that exist as solids at room temperature.
4. Iron containing prosthetic group in hemoglobin and the cytochromes.
5. Nutrasweet™ is the commercial name of this substance.
6. Metal ion integral in neurotransmission, intracellular communication, and development of bone structure.
7. One example of a steroid compound.
8. Ester in which all three hydroxy groups on glycerol have been esterified by saturated or unsaturated fatty acids.

9. Member of a group of organic compounds essential in the diet in small amounts.
10. Additive that makes white sugar into brown sugar.

Answers: 1. CARBOHYDRATE 2. PROTEIN 3. FATS 4. HEME 5. ASPARTAME 6. CALCIUM 7. CHOLESTEROL 8. TRIGLYCERIDE 9. VITAMIN 10. MOLASSES

3. See cartoons at end of module.

MEDIA

1. Nutrition, by MECC (Minnesota Educational Computer Consortium, St. Paul, MN 55165)—Computer program that takes a day's meals and calculates calories, fat, protein, carbohydrate, vitamins, and minerals. The program also gives suggestions for altering your diet.
2. TVO Video (TV Ontario) cassette. *Organic Chemistry 2: Industrial Applications* has programs on soaps and detergents, cosmetics, glues, and fibers. Other cassettes: *From Rags to Britches* (artificial fibers); *Is it Soup Yet?* (cooking); *Hair: the Untold Story*; and *You are What You Eat*, TV Ontario Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516; (800) 331-9566.
3. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

   For the Apple II computer: AP 1522

Links/Connections

WITHIN CHEMISTRY

Biochemistry and Metabolism
Analytical Chemistry
Oxidation-Reduction
Chromatography
Solubility
Synthetic Chemistry

Lipids. Approximately 35-40% of the total calories taken by an average adult comes in the form of dietary lipids. Oxidation of lipids is well studied by chemists because this reaction is related to lipid deterioration and production of undesirable breakdown products. Crystalline properties of fats are important in formulations of ice creams, margarines, mayonnaise, and many other common food products. Hydrogenation of lipids is important in the food industry because degree of unsaturation is directly proportional to rate of oxidation. A study of emulsification of fats leads to studies in numerous areas of chemistry: crystal polymorphism, surface tension, van der Waals attraction, electrostatic repulsion, electric double layers, adsorption at interfaces, liquid crystals, complex formation.

Proteins. The basic chemistry of proteins is always related to their functionality. For example, the chemistry of muscle contraction is related to rigor mortis and postmortem tenderness of meat. The unfolding and refolding of the helical chains in collagen help explain formation of gelatins. Chemical changes in proteins during food storage and processing can lead to unwanted breakdown products, with consequent alteration of nutritional quality.

Carbohydrates—Monosaccharides and Oligosaccharides. The many flavor compounds in foods are the results of the degradation and subsequent rearrangements and reactions of monosaccharides and oligosaccharides. The reaction mechanisms of these reactions have been extensively studied. Polysaccharides are important in food chemistry because of their unique gelling characteristics. Gelling of polysaccharides often requires complexation with metal ions, and the degree and nature of the substituent groups also plays an important role.

Vitamins and Minerals. Vitamins are essential for the proper functioning of the body. They cannot be biosynthesized by human beings and therefore must be part of the diet. About a dozen different vitamins have been identified, two-thirds of which are water- soluble and one-third of which are fat-soluble. The water-soluble vitamins wash out through the action of the body's aqueous disposal system, and thus must be included in the daily diet. On the other hand, the fat-soluble vitamins can be stored in the adipose tissues and can leach into the blood stream as needed. In fact, the fat-soluble vitamins tend to accumulate, sometimes to toxically high levels if ingested in excess. Essential minerals can be divided for convenience into macrominerals (Ca, Cl, Mg, Na, K, P and S) and trace minerals (Cr., Co, Cu, F, I, Fe, Mn, Mo, Ni, Se and Zn). All are essential in the diet and lead to deficiency conditions if lacking or in short supply in the diet. *ChemCom* (2nd ed.) provides an excellent section on vitamins and minerals, including a Vitamin C laboratory activity. See *ChemCom* (1993) in the *References*. (Idea contributed by Angie Matamoros.)

Kitchen Chemistry. Kneading dough is a chemical reaction. During kneading and subsequent resting periods, disulfide bonds in the wheat protein, which is 80% gluten, undergo reduction and subsequent reoxidation. The initiation of reduction in dough-mixing is thought to be due to thiol-disulfide exchange and possible formation of free radicals. Disulfide reduction physically loosens the gluten and facilitates better interaction with the starch, lipids and other additives to form a continuous network complex.

Fertilizers. Because of fertilizer losses in the field, energy requirements and environmental concerns, alternative sources of ammonia are being explored. Technology is being developed to make more efficient use of fertilizers, particularly nitrogen fertilizers to control nitrification so that nutrients can be made available to plants on a need-supply schedule (see *Industrial Inorganic Chemistry* module).

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

Medicine
Nutrition
Advertising
Business
Chemical industry
Food Science
Home Economics

Biology. To meet the world's nitrogen requirements, biologists are attempting to exploit nitrogen-fixing bacteria and blue-green algae that live in fields, forests, and oceans.

Animal Production. Chemists can make a major contribution to animal production by developing (a) new sources of nonprotein nitrogen that are effective, safe, and inexpensive to use in the diets of forage animals, and (b) acceptable growth stimulants for use in animal feeds.

Fish Production. Research can be expanded to improve fish feeds, control fish diseases, and develop sex-controlling chemicals. Aquaculture technology in the tropics and subtropics can help alleviate food shortages—fish are extremely efficient converters of feed into proteins. There are many opportunities for chemists to contribute to fish production research.

Chemists can contribute in the following areas of food processing and production:

> **Food additives**. Additives facilitate processing, handling, distribution, and preparation of foods in the home; they control chemical, physical, and biological changes; they extend shelf life of foods; and they improve sensory and nutritive properties. Without additives, there would be few convenience foods, and certain fresh fruits and vegetables would not be available year round. The search for effective additives from natural sources is the domain of the natural products chemist.
>
> **Food processing and preservation**. Nitrites have, in the past, been added to smoked and cured meats to improve color and to inhibit the growth of the toxic botulism organism. Nitrite additives are no longer acceptable because under

certain conditions of heating and storage, they react with other constituents of the food to produce minute quantities of nitrosamine, which is carcinogenic in rats. Chemists are engaged in a research program to determine the mechanism by which nitrites inhibit botulism, and with this information, to develop safe alternative preservatives.

Development of unconventional sources of food and feed. In modern times, various attempts have been made to use microbial cell mass, sometimes called SCP (single-cell protein) as a major protein source. Research chemists have found ways to couple certain carbon source substrates, such as methanol, methane, and wood hydrolyzate, with the appropriate microorganisms to produce SCPs for a variety of uses. Presently, major constraints in the widespread use of SCPs are economics (production costs are considerable and vary with the raw material), medical problems (nucleic acids in yeast have been found to increase blood uric acid levels, leading to an increase of gout), and nutritional limitations (high nucleic acid levels and low levels of two essential amino acids, methionine, and tryptophan).

Psychology. Relationship of eating disorders to nutritional needs.

TO THE CONTEMPORARY WORLD

Personal

Informed consumerism

Analysis of diet

Knowing the best foods to eat

Assessment of advertising

Community

1. **Field trips**: fish hatchery, local food processing plant, dairy, sewage treatment plant
2. **Knowledgeable individuals**: nutritionist, dietitian

Societal

1. Making decisions on food safety. Library research on key considerations regarding the food supply. Criteria include scientific evidence, social value, economic impact, the decision structure and political acceptability.
2. Evaluating benefits and risks under the law. What are "safe" levels for food additives? Should persistent pesticides (such as DDT) be replaced with more toxic, but less persistent ones? Has the replacement of trichloroethylene with methylene chloride as an extracting solvent resulted in enhancement of human health?
3. Life-style, eating, and health care. The relationship between diet and disease.
4. Nutritional risk and life expectancy: hunger and malnutrition. Worldwide hunger problem. When to intervene? Political, ethical, economic, scientific, medical aspects.
5. Dietary assessment: Food ecology—nature, nurture, and nutriture.
6. What is food and what is poison?

Extensions

Any one of the topics listed under Links and Connections would make a suitable research paper for a group or individual for honors projects, and with suitable guidance, for a laboratory research project (or an interdisciplinary research project). The topic of *Food and Chemistry* cuts across virtually every aspect of human endeavor. It is a rich area to explore on many levels.

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Module drafted by Jennifer Hubert, Jane A. Miller and Marie C. Sherman, the Missouri team.

Agricultural Research Service. (1979). *Composition of foods.* U.S. Department of Agriculture.

Resource for *Activity 1: Analysis of Salt in Snack Food.*

American Chemical Society. *ChemCom (Chemistry in the Community)*, 2nd ed. (1993). Dubuque: Kendall/Hunt Pub. Co.

Chemistry text developed by the American Chemical Society that links study of chemistry with contemporary societal issues.

American Public Health Association. (1965). *Standard methods for the examination of water and wastewater.* New York: American Public Health Association.

Resource for *Activity 1: Analysis of Salt in Snack Food.* Address: American Public Health Association, 1740 Broadway, New York, NY, 10019.

Bergandine, D.R., Jones, L. and Frederick, B. (1991, March). The chemistry of fitness. *The Science Teacher*, 29-32.

Blumenthal, D. (1990, May). Red no. 3 and other colorful controversies. *FDA Consumer, 24*(4), 18-21.

Resource for *Activity 2: Chromatographic Comparison of M&M™ Candy with Reese's Pieces™.*

Bodanis, D. (1986). *The secret house.* New York, NY: Simon and Schuster.

Borer, L. *et al.* (1994, May). The chemistry of coffee. *The Science Teacher*, 36-38.

Committee on Chemistry and Public Affairs. (1980). *Chemistry and the food system.* Washington, DC: American Chemical Society.

Report generated to enhance public understanding of the food system from farm to table. The report describes how chemical substances have provided benefits in production, storage and processing of foods; it also includes some of the disadvantages, problems and risks involved.

Damon, G. E., and Javssen, W. F. (1973, July-August). Additives for eye appeal. *FDA Consumer, 7*(6), 15-18.

Resource for *Activity 2: Chromatographic Comparison of M&M™ Candy with Reese's Pieces™.*

Eckstein, E. F. (1980). *Food, people, and nutrition.* Westport, CT: AVI Publishing Co.

Unique nutrition textbook that includes approaches to nutrition on the whole body level, the cellular level, and the life cycle level. Questions regarding malnutrition in a land of plenty raise societal issues that would make interesting research problems and discussion topics.

Florman, M., and Florman, M. (1990). *Fast foods eating in and eating out.* Yonkers, NY: Consumers Union.

Friedstein, H. G. (1983). Basic concepts of culinary chemistry. *Journal of Chemical Education*, 60, 1037.

Hillman, H. (1989). *Kitchen science.* Boston, MA: Houghton Mifflin.

Compendium of information for cooks written in a catechism question-and-answer style. Questions range all the way from the best way to kill a lobster to causes of discoloration of foods. Some chemical names, but no formulas.

Korchin, F. G. (1983). *Science in the marketplace.* Red Bank, NJ: Tiger Publications.

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Markow, P. G. (1988). Ideal solvent for paper chromatography of food dyes. *Journal of Chemical Education, 65,* 899-900.

Piscatella, J. C. (1987). *Don't eat your heart out cookbook.* New York, NY: Workman.

A resource for *Activity 1: Analysis of Salt in Snack Food.* (Publisher's address: Workman Publishing, 708 Broadway, New York, NY 10003.)

Selinger, B. (1989). *Chemistry in the marketplace.* New York, NY: Harcourt Brace Jovanovich.

Tocci, S. (1987). *Chemistry around you.* New York, NY: Prentice Hall.

Wong, D. W. S. (1989). *Mechanism and theory in food chemistry.* New York, NY: Van Nostrand Reinhold.

Reference work that focuses on the reaction mechanisms and theories essential to understanding the many chemical processes that occur in foods and food systems. The emphasis is on the interactions among food constituents that correlate with the chemistry of individual food systems.

There are many articles concerning household chemistry in *ChemMatters, Journal of Chemical Education, FDA Consumer*, and *Chemical and Engineering News.* These are a few examples of these articles.

Baugh, M. (1989). Oil changes. *ChemMatters, 7*(4), 7-9.

Benson, K. D. (1990). Fast fat. *ChemMatters, 8*(1), 13-15.

Blumenthal, D. (1990). Red dye no. 3 and other colorful controversies. *FDA Consumer, 24*(4), 18-21.

Emsley, J. (1988). Artificial sweeteners. *ChemMatters, 6*(1), 4-8.

Farley, D. (1990). Keeping up with the microwave revolution. *FDA Consumer, 24*(2), 17-21.

Glover, D. (1990). The margarine puzzle. *ChemMatters, 8*(3), 16.

Marmion, D. M. (1979). *Handbook of U.S. colorants for foods, drugs, and cosmetics* (pp. 53-93). New York, NY: John Wiley.

McCamish, M. (1987). The rise of self-rising flour. *Journal of Chemical Education 64,* 710-12.

McKone, H. T. (1990, October). Copper in the candy, chromium in the custard. *Today's Chemist, 3*(5), 22-25, 34.

Pomeranz, Y., Finney, K. F., and Hoseney, R. C. (1978). Molecular approach to breadmaking. *Science, 167,* 944-949.

Staten, V. (1993). Can you trust a tomato in January? The hidden life of groceries and other secrets of the supermarket revealed at last. New York: Simon and Schuster Touchstone Book.

Stehlin, D. (1991). Women and nutrition. *FDA Consumer, 25* (1), 11-13.

Artificial Fat Information

Olestra Professional and Technical Relations, 2 Procter and Gamble Plaza, Cincinnati, OH 45202.

The NutraSweet Company Consumer Affairs Center, Box 830 Deerfield, IL 60015; 1-800-321-7254 (9 AM - 3 PM, CST).

Nutritional Analysis

Important Nutritional Information About McDonald's® Menu. Pamphlet No. 9. (1990). McDonald's Nutrition Information Center, McDonald's Corporation, Oak Brook, IL 6052. (708) 575-FOOD.

U.S. Department of Agriculture Food Pyramid. Contact Regional Office, Food and Nutrition Service, U.S. Department of Agriculture (in local telephone book) for a copy. The Food Pyramid was publicized in the summer of 1992. It replaces the previous five suggested food groups as suggestions for healthy eating.

Regional Offices, U.S. Department of Agriculture Food and Nutrition Service

Mid-Atlantic Regional Office
Mercer Corporate Park
CN 02150, Trenton, NJ 08650
(609) 259-5146; (609) 348-5146

Midwest Regional Office
50 East Washington Street
Chicago, IL 60602
(312) 886-5307

Mountain Plains Regional Office
2420 West 26th Avenue, Suite 430-D
Denver, CO 80211
(303) 964-0330

Northeast Regional Office
33 North Avenue
Burlington, MA 01803
(508) 272-8833; (508) 223-0280

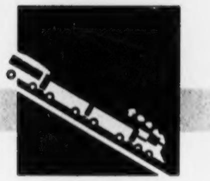
Southeast Regional Office
1100 Spring Street, NW
Atlanta, GA 30309
(404) 881-4028

Southwest Regional Office
1100 Commerce Street
Dallas, TX 75242
(214) 729-0204

Western Regional Office
550 Kearney Street, Room 400
San Francisco, CA 94108
(415) 556-4939

The National Dairy Council provides informational films and materials on request. To access the unit nearest you, contact the National Dairy Council, 6300 North River Road, Rosemont, IL 60018-4233; (312) 696-1860, ext. 220.

Appendix



- **Transparency Masters**
    1. McDonald's Nutritional Analysis I
       McDonald's Nutritional Analysis II
    2. Food Additives and Examples
    3. Analyzing Foodstuffs for Food Additives
    4. Word Search
- **Humor**

McDonald's Nutritional Analysis I
USRDA (U.S. Recommended Daily Allowance)

Sandwiches *Nutrition Information per Serving*

Item	Hamburger		Cheeseburger		Quarter Pounder®		Quarter Pounder w/cheese®		Big Mac®		Filet-O-Fish®		McD.L.T.®		McChicken®	
	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA
Serving Size (g)	102		116		166		194		215		142		234		190	
Calories	260		310		410		520		560		440		580		490	
Protein (g)	12.3	20	15	25	23.1	35	28.5	45	25.2	40	13.8	20	26.3	40	19.2	45
Carbohydrate (g)	30.6		31.2		34		35.1		42.5		37.9		36		39.8	
Fat (g)	9.5		13.8		20.7		29.2		32.4		26.1		36.8		28.6	
Mono-unsaturated fatty acids (g)	5.09		7.66		11.38		16.51		20.90		10.22		16.7		11.5	
Poly-unsaturated fatty acids (g)	0.77		0.93		1.21		1.51		1.50		10.76		8.5		11.6	
Saturated fatty acids (g)	3.63		5.17		8.09		11.18		10.05		5.16		11.5		5.4	
Cholesterol (mg)	37		53		86		118		103		50		109		42.6	
Sodium (mg)	500		750		660		1150		950		1030		990		780	
Vitamin A Activity (IU)	152	4	392	8	223	4	703	15	352	8	146	2	754	15	104	2
Vitamin C (mg)	2.15	4	2.15	4	3.24	6	3.24	6	1.68	2	0.06		7.38	10	2.42	4
Thiamin (mg)	0.28	20	0.29	20	0.36	25	0.37	25	0.48	30	0.30	20	0.39	25	0.96	60
Riboflavin (mg)	0.16	10	0.21	15	0.29	15	0.39	20	0.41	25	0.15	8	0.36	20	0.21	15
Niacin (mg)	3.84	20	3.86	20	6.70	35	6.73	35	6.81	35	2.68	15	6.87	35	8.92	45
Calcium (mg)	121.65	10	198.51	20	141.74	15	295.46	30	255.95	25	164.84	15	225.30	25	142.62	15
Iron (mg)	2.29	15	2.3	15	3.68	20	3.72	20	4	20	1.83	10	3.91	20	2.61	15

Soft Drinks *with ice*

	Coca-Cola Classic®				Orange Drink				Sprite®				Diet Coke®			
	12 Fl Oz	16 Fl Oz	22 Fl Oz	32 Fl Oz	12 Fl Oz	16 Fl Oz	22 Fl Oz	32 Fl Oz	12 Fl Oz	16 Fl Oz	22 Fl Oz	32 Fl Oz	12 Fl Oz	16 Fl Oz	22 Fl Oz	32 Fl Oz
Carbohydrate (g)	38	50	70	101	33	44	60	88	36	48	66	96	0.3	0.4	0.5	0.6
Calories	140	190	260	380	130	180	240	360	140	190	260	380	1	1	2	3
Sodium (mg)	15	20	25	40	10	20	20	25	15	20	25	40	30	40	60	80

McDonald's Nutritional Analysis II

Other Items *Nutrition Information per Serving*

Item	Small French Fries		Medium French Fries		Large French Fries		Apple Pie		Vanilla Lowfat Milk Shake		Chocolate Lowfat Milk Shake		Strawberry Lowfat Milk Shake	
	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA
Serving Size (g)	68		97		122		83		293		293		293	
Calories	220		320		400		260		290		320		320	
Protein (g)	3.13	4	4.44	6	5.61	8	2.2	4	10.8	15	11.6	20	10.7	15
Carbohydrate (g)	25.6		36.3		45.9		30		60		66		67	
Fat (g)	12		17.1		21.6		14.8		1.3		1.7		1.3	
Mono-unsaturated fatty acids(g)	6.49		9.21		11.64		9.11		.67		.92		.64	
Poly-unsaturated fatty acids (g)	0.50		0.70		0.89		0.87		.05		.05		.05	
Saturated fatty acids (g)	5.05		7.17		9.06		4.83		.63		.76		.63	
Cholesterol (mg)	9		12		16		6		10		10		10	
Sodium (mg)	110		150		200		240		170		240		170	
Vitamin A Activity (IU)	0		0		0		0		306	6	306	6	306	6
Vitamin C (mg)	8.16	15	11.64	20	14.64	25	11.40	20	0		0		0	
Thiamin (mg)	0.14	10	0.19	15	0.24	15	0.06	4	0.13	8	0.13	8	0.13	8
Riboflavin (mg)	0		0		0		0.02		0.48	30	0.50	30	0.48	30
Niacin (mg)	1.84	10	2.60	15	3.29	15	0.32		0.31		0.40	2	0.31	2
Calcium (mg)	9.93		14.10		17.81		10.65		327.24	35	332.48	35	327.31	35
Iron (mg)	0.52	2	0.73	4	0.93	6	0.71	4	0.10		0.84		0.09	

Item	Lowfat Frozen Yogurt Cone		Strawberry Lowfat Frozen Yogurt Sundae		Hot Fudge Lowfat Frozen Yogurt Sundae		Hot Caramel Lowfat Frozen Yogurt Sundae		McDonaldland Cookies		Chocolaty Chip Cookies	
	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA	Amount	%USRDA
Serving Size (g)	86		171		169		174		56		56	
Calories	100		210		240		270		290		330	
Protein (g)	4	6	5.7	8	7.3	10	6.6	10	4.2	6	4.2	6
Carbohydrate (g)	22		49.2		50.5		59.3		47.1		41.9	
Fat (g)	0.75		1.1		3.2		2.80		9.2		15.6	
Mono-unsaturated fatty acids(g)	0.28		0.39		0.76		1.22		6.80		10.17	
Poly-unsaturated fatty acids (g)	0.06		0.04		0.05		0.09		0.52		0.39	
Saturated fatty acids (g)	0.41		0.63		2.35		1.51		1.85		5.04	
Cholesterol (mg)	3		5		6		13		0		4	
Sodium (mg)	80		95		170		180		300		280	
Vitamin A Activity (IU)	128	2	214	4	214	4	291	6	0		0	
Vitamin C (mg)	0		1.3	2	0		0		0		0	
Thiamin (mg)	0.04	2	0.07	4	0.08	6	0.08	6	0.25	15	0.18	10
Riboflavin (mg)	0.18	10	0.29	20	0.35	20	0.35	20	0.18	10	0.21	10
Niacin (mg)	0.37	2	0.25		0.30		0.26		2.54	10	2.47	10
Calcium (mg)	112	10	190.46	20	235.13	25	221.77	20	8.91		23.92	2
Iron (mg)	0.23		0.16		0.48	2	0.08		2.07	10	2.18	10

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Food Additives and Examples

Additive Type	Purpose	Examples
Nutrient	Improve nutritive value	Vitamins and minerals; iodine in iodized salt, B vitamins in enriched flour
Flavoring agents	Add or enhance flavor	Salt, monosodium glutamate (MSG), spices
Preservatives, antimycotic agents (growth inhibitors)	Prevent spoilage, microbial growth	Propionic acid, sorbic acid, benzoic acid, and salt retard mold growth on cheese, bread; sodium nitrite in meats adds to flavor, maintains pink color, and prevents growth of *Clostridium botulinum*
Antioxidants	Prevent fat rancidity	BHA and BHT react with free radicals to prevent oxidation of unsaturated fats
Coloring agents	Increase visual appeal	Carotene—natural yellow color added to butter and margarine, converted to vitamin A in the body; synthetic dyes
Leavening agents	Make foods light in texture	Baking powder and baking soda produce CO_2 that expands food as it cooks
Bleaches	Whiten foods such as flour and cheese; hasten maturing of cheese	SO_2 bleaches, disinfects, and preserves dried foods; seems safe in foods except for persons allergic to it
Emulsifiers	Give texture, smoothness, other desired consistencies; stabilize oil-water mixtures	Cellulose gums, dextrins in whipped cream, cake mixes, mayonnaise
Anticaking agents	Keep foods free flowing	Sodium ferrocyanide added to salt to prevent caking
Humectants	Retain moisture	Glycerin
Sweeteners	Impart sweet taste	Sugar (sucrose), dextrin, fructose, saccharin, aspartame, sorbitol, mannitol

Analyzing Foodstuffs for Food Additives
(or is that stuff really in my food?)

DIRECTIONS: While looking at the ingredients section of food labels, find two examples for each of the 11 categories of food additives shown below. You may use the same label for more than one category. If the label lists the specific name of the additive, write the name underneath the product name.

	Example 1	**Example 2**
Nutrients		
Flavoring agents		
Preservatives		
Antioxidants		
Coloring agents		
Leavening agents		
Bleaches		
Emulsifiers		
Anticaking agents		
Humectants		
Sweeteners		

Word Search

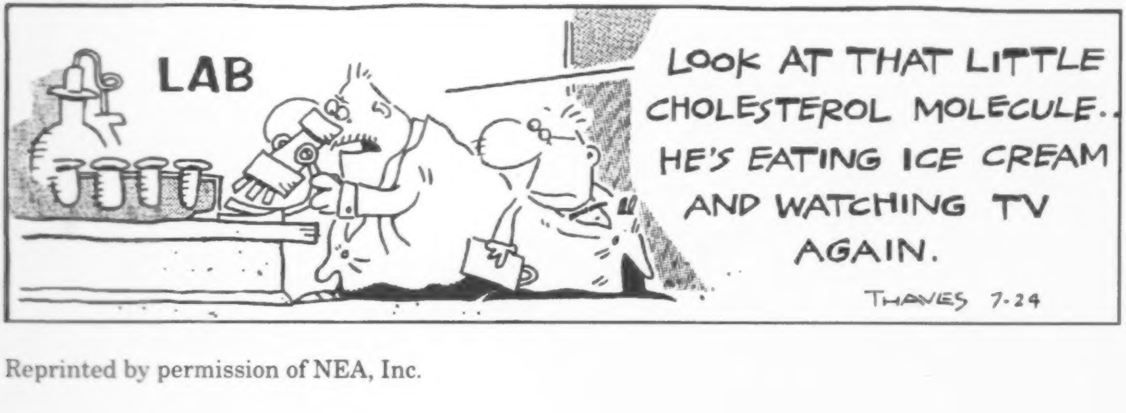
```
A D C A M X N A C E E X O E O Q C
F F G Z F A T S F T D U Y I Z A N
R L L A R U R P U F I N P L R M T
I O M U I C L A C X R U V B W M U
K R K S Z F W R P F E S O G T O V
M E C J D S J T E Q C H O K W L W
Y T N N L W P A D T Y P E C Q A I
T S X I N Z R M F D L M J M Z S B
T E Q F M J N E R U G W H L E S M
A L D U M A R A A S I F M O V E H
L O T K R U T K I W R I B P J S N
O H D A U E S I K V T P G X W V O
T C Z U F G A B V B N I E T O R P
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Polyhydroxy aldehyde or ketone.
2. Peptide with more than 100 amino acid residues.
3. Lipids that exist as solids at room temperature.
4. Iron containing prosthetic group in hemoglobin and the cytochromes.
5. Nutrasweet™ is the commercial name of this substance.
6. Metal ion integral in neurotransmission, intracellular communication, and development of bone structure.
7. One example of a steroid compound.
8. Ester in which all three hydroxy groups on glycerol have been esterified by saturated or unsaturated fatty acids.
9. Member of a group of organic compounds essential in the diet in small amounts.
10. Additive that makes white sugar into brown sugar.

CHEMTECH, April 1980, p. 237. © American Chemical Society. Reprinted with permission.

FRANK AND ERNEST © **by Bob Thaves**


LAB
LOOK AT THAT LITTLE CHOLESTEROL MOLECULE.. HE'S EATING ICE CREAM AND WATCHING TV AGAIN.
THAVES 7-24

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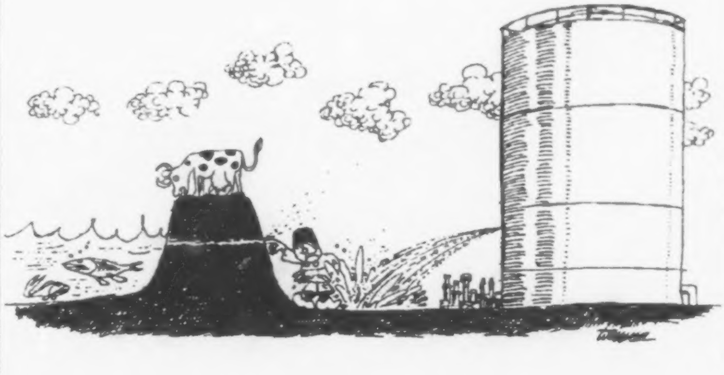
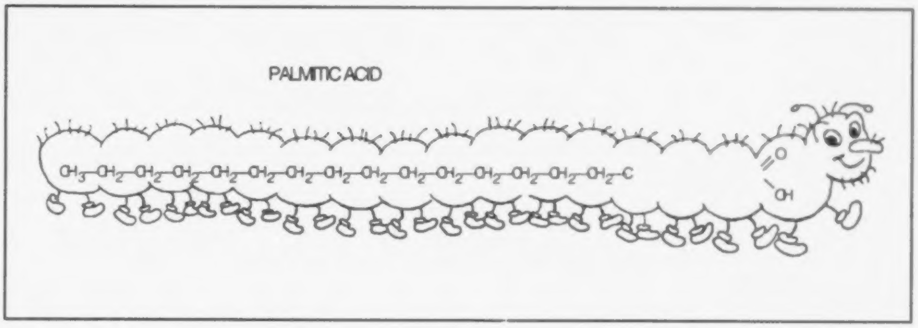
86

"Now that I've satisfied 10% of my minimum daily requirements . . . a toast to the beautiful women of science."

CHEMTECH, September 1980, p. 538. ©American Chemical Society. Reprinted with permission.



CHEMTECH, November 1972, p. 642. © American Chemical Society. Reprinted with permission.


PALMITIC ACID
CH3–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–C
O
OH

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ZIGGY...
by Tom Wilson
BONJOUR!
HI!...WHAT'S THE SOUP OF THE DAY?
MENU
MUSHROOM & CALCIUM CASEINATE! ...C'EST MAGNIFIQUE!
MENU
SIR...MIGHT I RECOMMEND YOU BEGIN WITH OUR "MUSHROOM & CALCIUM CASEINATE SOUP"...THIS IS SERVED WITH A HEARTY SUPPLY OF BLEACHED, BROMATED WHEAT CRACKERS!
...THEN "ASPARAGUS AND MEATBALL REPLICATA"— A TANTALIZING BLEND OF SOYBEAN CURD AND FRESH HYDROLYZED VEGETABLE PROTEIN!
...AND AS THE GRAND FINALE TO THIS CULINARY MAJESTY, WE PROUDLY OFFER "FACSIMILE DU LEMON PIE." FUMARIC ACID AND DISODIUM PHOSPHATE LOVINGLY BLENDED WITH YELLOW DYE #5 AND NUDGED BEYOND PERFECTION BY THE ADDITION OF IMPORTED MONO GLYCERIDE.
GOSH! YOU MAKE IT SOUND JUST DELICIOUS! I'LL HAVE THAT!
VERY GOOD, SIR!
LATER
EXCELLENT! MY COMPLIMENTS TO THE CHEF!
...OF COURSE, SIR!
H2O

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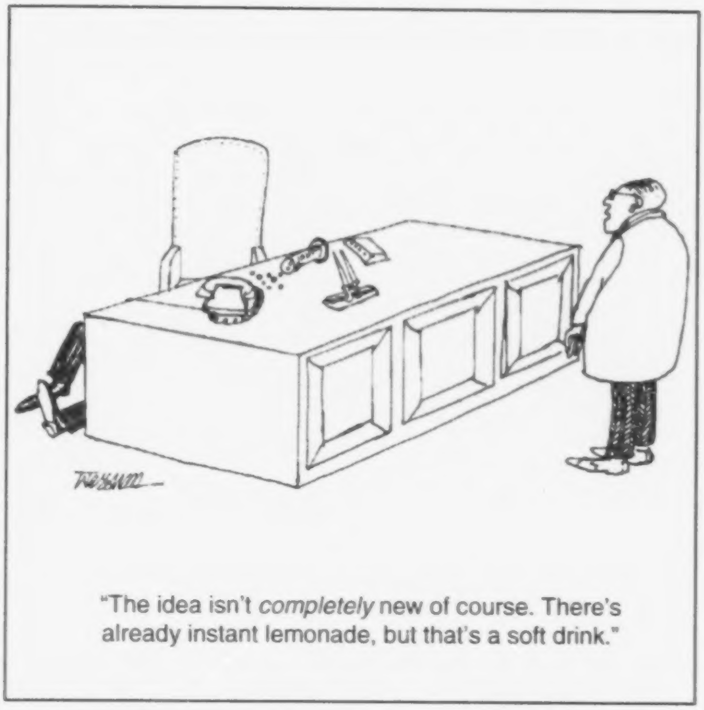

"The idea isn't *completely* new of course. There's already instant lemonade, but that's a soft drink."

CHEMTECH, March 1974, p. 168. © American Chemical Society. Reprinted with permission.

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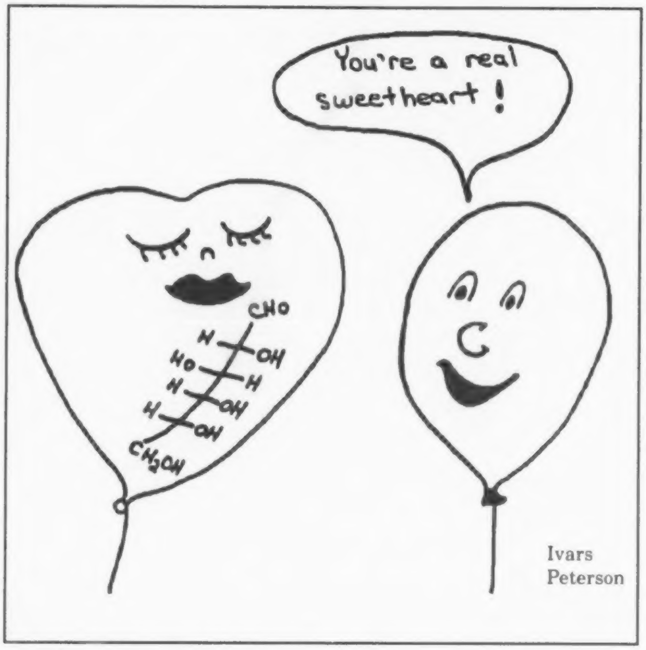

CHEM 13 NEWS, January 1983, p. 2. Reprinted with permission.

Stone-Ground Corn
stone-ground calcium propionate added to retard spoilage
S. Harris

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REMEMBER, WHILE IT'S SIMMERING, ADD THE WHITE WINE, A HALF-CUP OF LIGHT CREAM AND A FEW DICED SHALLOTS.
THROW IN A HANDFUL OF SALT.
S. harris

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Shelly
ZAP!
"WELL I JUST DON'T KNOW. IT SEEMS A LITTLE UNETHICAL TO CREATE LIFE USING ELECTRICITY INSTEAD OF LIPIDS, CARBOHYDRATES, PROTEINS AND NUCLEIC ACIDS"

Cartoon by Shelly Fischman. Reprinted with permission.

"OF COURSE IT'S SAFE. IT HAS NO PRESERVATIVES, NO ADDITIVES, NO ARTIFICIAL COLORING..."

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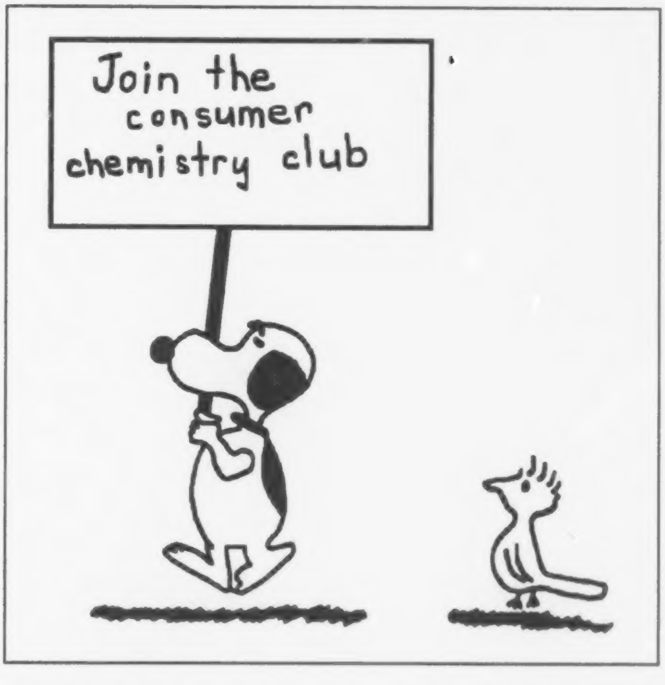
Join the consumer chemistry club

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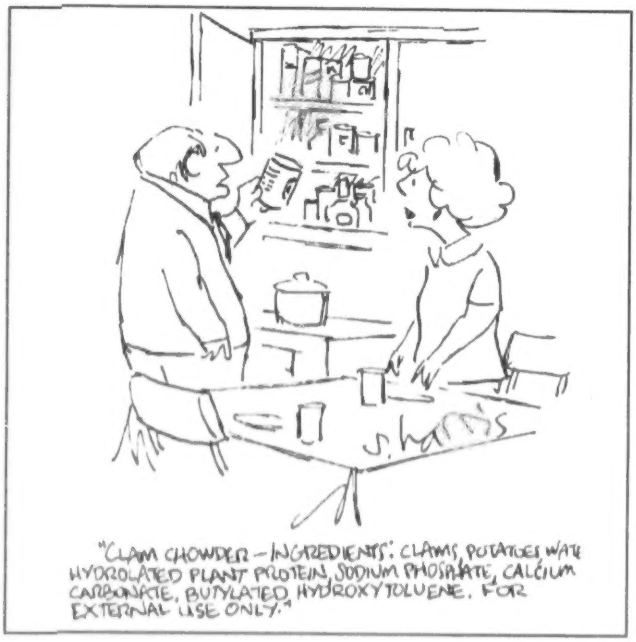
s. harris
"CLAM CHOWDER — INGREDIENTS: CLAMS, POTATOES, WATER, HYDROLATED PLANT PROTEIN, SODIUM PHOSPHATE, CALCIUM CARBONATE, BUTYLATED HYDROXYTOLUENE. FOR EXTERNAL USE ONLY."

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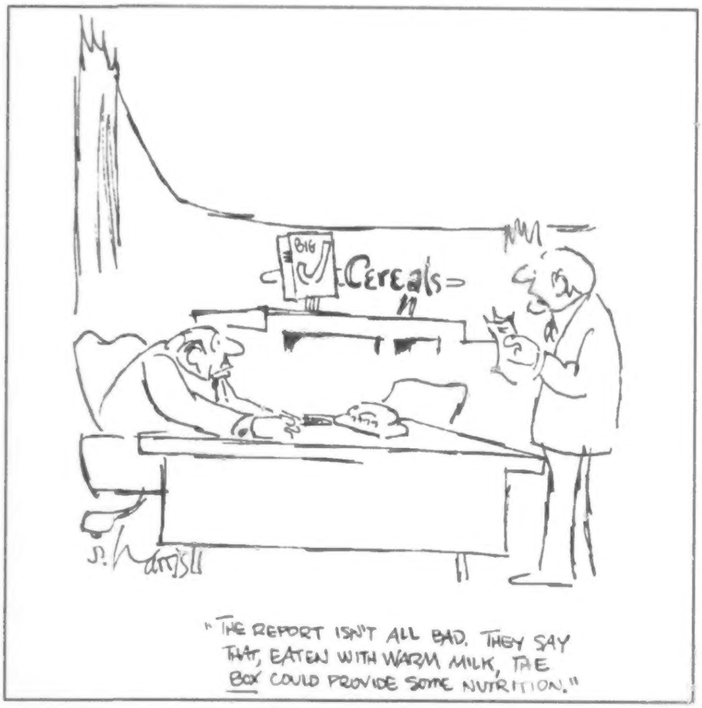
BIG
Cereals
S. Harris
"THE REPORT ISN'T ALL BAD. THEY SAY THAT, EATEN WITH WARM MILK, THE BOX COULD PROVIDE SOME NUTRITION."

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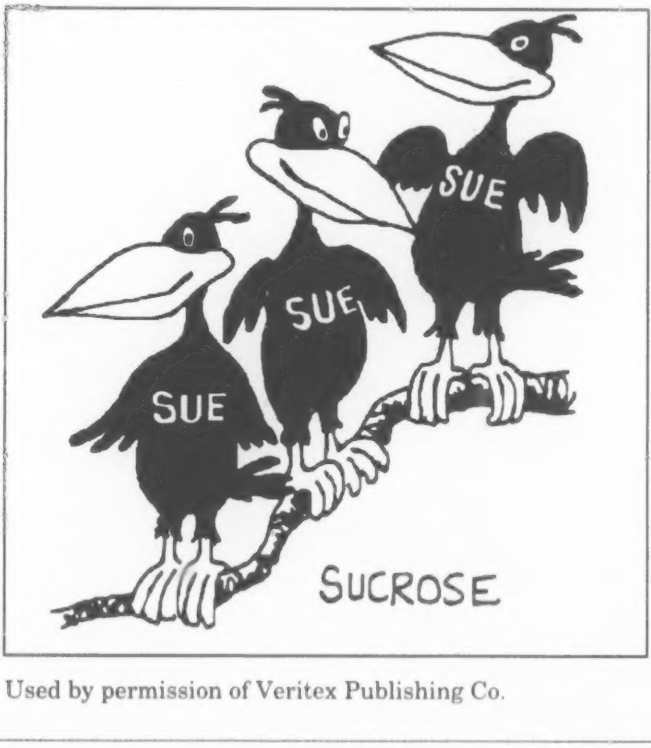
PHON
ST
K
UWE
I DON'T CARE IF YOU ARE KAPTAIN KARCINOGEN. I WANT MY HAMBURGER BACK!!!

CHEM 13 NEWS, May 1979, p. 5. Reprinted with permission.



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GONDWANA UNIVERSITY
Shelly ©89
NOW YOU JUST LISTEN HERE MR. "KING OF CARNIVORES"......YOUR CHOLESTEROL COUNT IS TOO HIGH AND YOU'RE DEVELOPING GOUT. AS OF THIS MINUTE, RED MEAT IS OUT OF YOUR DIET!

Cartoon by Shelly Fischman. Reprinted with permission.

A SourceBook Module

Version 2.0 1994

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New Rochelle, NY 10805
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FAX: (914) 654-5387

FORENSIC CHEMISTRY

ChemSource

Instructional Resources for Preservice and Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

In running a routine route through a lighted park, a jogger was beaten and robbed by an attacker. There was a struggle and both people rolled on the ground. At the scene the investigating officer obtained a description of the attacker, discovered small pieces of glass, and noticed blood stains on the ground. The blood was determined to be of human origin and was *identified* as the victim's blood.

The victim picked out a suspect from a lineup, and the suspect's apartment was searched. The officers found a broken lens in the suspect's eyeglasses. The glass fragments found in the park *matched* the glass in the broken lens. A jacket was also examined. Soil particles were found embedded in the fabric. The soil found in the jacket was *compared* with the soil in the park area and was determined to be *identical*. Blood, glass, and soil are physical evidence. **Physical evidence** is anything that is found at the crime scene, including the victim and/or the suspect.

The forensic chemist's task is to assist the court in deciding whether physical evidence can be tied to a given individual. Evidence may also help exonerate an innocent person. This assistance allows the court to decide whether or not the particular individual has been involved in a crime.

The *examination* of physical evidence by a forensic chemist is usually undertaken for *identification* (Is it blood? Is it human blood?) or *comparison* (Does the crime specimen of blood match the suspect's blood specimen?). A variety of physical and chemical tests and sophisticated analytical instrumentation assist the forensic scientist in associating physical evidence with the suspect.

This module will provide teachers with an introduction to the kinds of physical evidence, physical and chemical tests, and analytical techniques that are routinely used by forensic chemists to associate or dissociate a suspect with a crime. Forensic science is an excellent example of the interdisciplinary nature of real science. It includes concepts from chemistry, physics, biology, and geology.

PLACE IN THE CURRICULUM

This module can be used toward the end of the second semester of the one-year course in chemistry. Because it concerns the application of chemistry to a topic of interest to many students, it serves as an example of a career opportunity utilizing science, in general, and chemistry, in particular.

CENTRAL CONCEPTS

1. Forensic science is the application of science to law.
2. The forensic scientist skillfully applies the principles and techniques of chemistry, biology, geology, and many other fields as well (physics, mathematics, *etc.*) to the analysis of the many types of evidence.
3. Evidence includes glass and soil samples, tire marks, blood, hair, drugs, fibers, firearms, bullets and cartridges, documents, indented writings, erasures, burned documents, body fluids, fingerprints, voice prints, and many other things.
4. The examination of physical evidence is undertaken for identification or comparison.

5. The process of identification determines a substance's physical or chemical identity with as much certainty as the employed analytical technique permits.
6. A comparative analysis subjects suspect and control specimens to the same tests and examinations for the purpose of determining whether they have a common origin.
7. Physical and chemical tests are used by forensic scientists. In chemistry, tests include density determination, elemental composition, chemical reactivity, and the determination of optical properties such as color. Biological tests include fingerprints, hair analysis, and blood identification. Tests involving physics include comparison of sound wave patterns, accident reconstruction, and index of refraction. In geology, soil analysis is studied. Instrumentation is an important aspect of the tests.
8. Modern analytical instruments available for identification and comparison include gas chromatography, thin layer chromatography, high performance liquid chromatography; infrared, ultraviolet, and mass spectroscopy; atomic absorption spectroscopy, and electrophoresis (see *Instrumentation* module).

RELATED CONCEPTS

1. Metric measurements
2. Density
3. Index of refraction
4. Chromatography
5. Chemical tests for anions and cations

RELATED SKILLS

1. Careful observation
2. Use of a microscope
3. Use of a balance and graduated laboratory glassware
4. Chemical separations

PERFORMANCE OBJECTIVES

After completing their study of forensic chemistry, students should be able to:

1. recognize the three primary activities of a forensic chemist: examination, identification, comparison.
2. see the interdisciplinary applications of forensic science to real life problems.
3. recognize the importance of modern instrumentation to solving problems.
4. list a number of careers that involve forensic science (firearms expert, medical examiner, museum curator, archaeologist, *etc.*).
5. identify and discuss a variety of separation techniques (see *Separations* module).
6. identify and discuss a variety of identification techniques.
7. use the above techniques to make reasonable comparisons.
8. provide possible physical and chemical explanations for these techniques used in forensic chemistry.

Concept/Skills Development

Laboratory Activity: Student Version

Activity 1: Drug Identification

Introduction

In this activity, you will identify a drug. Drug identification is a routine procedure for a medical technician working in a hospital trying to identify the source of drug overdose, or the law enforcement investigator trying to identify a suspected controlled drug, or for the medicinal chemist employed by a pharmaceutical manufacturer trying to discover why a competitor's product is more effective.

Drugs can be identified in a variety of ways: characteristic colors when treated with special reagents, formation of crystalline solids with characteristic color and crystal structure when treated with appropriate reagents, or thin layer chromatography (TLC). In TLC, a drug is identified by its R_f value and by its color when treated with various reagents or when observed under ultraviolet light.

Purpose

To determine the composition of several over-the-counter (OTC) drug formulations using TLC. The drugs to be tested are aspirin, acetaminophen, caffeine, and salicylamide.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Ethyl acetate and iodine vapors can be irritating.
3. Do not look at the ultraviolet light.

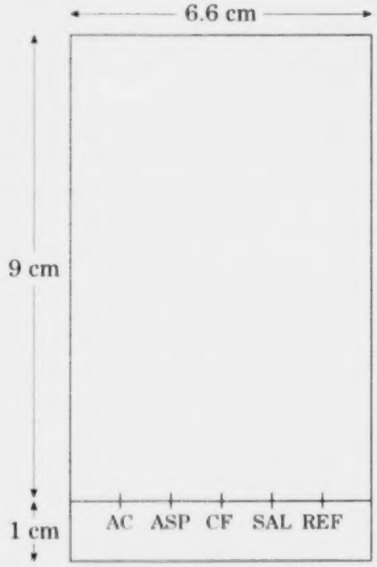


Figure 1. TLC plate.

Procedure

1. Obtain two precut (10 x 6.6 cm) TLC sheets. Do not touch the white surface and handle carefully only by the edges.
2. Using a lead pencil, draw a *light* line across the shorter dimension 1 cm from the bottom. Using a ruler as guide on the light line, mark off five equally spaced intervals on the line as shown in Figure 1.
3. Spot the sheet at each mark with the appropriate known solution: AC = Acetaminophen, AS = Aspirin, CF = Caffeine, SA = Salicylamide, and RF = Reference (Figure 2). These known solutions can be found in small reagent bottles. Use a melting point capillary tube or a wooden toothpick to spot the plate by dipping the tip of the tube (or toothpick) in the known solution and then touching the tip against the sheet at the appropriate mark. The applied spot should be no bigger than 1-2 mm. (Practice spotting on a piece of filter paper before spotting the TLC sheet.)

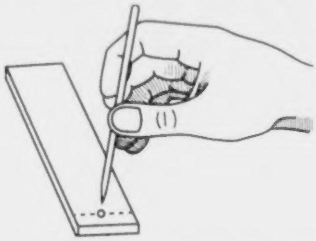


Figure 2. Spotting the TLC plate.

4. Obtain a one-pint (16 oz) canning jar with a screw-cap lid for the development chamber. It should contain a filter paper liner as shown in Figure 3. Add ethyl acetate to the jar to a depth of about 0.5 cm and swirl to moisten the paper liner. (*REMEMBER*: The level of the solvent must be below the spots on the sheet—5 mL solvent is usually enough). Place the spotted sheet in the development chamber so that it rests in the solvent and against the jar wall. Replace the jar's lid and allow the sheet to develop (about 20 min).
5. When the solvent has risen on the sheet to within 1 cm of the top, remove the sheet from the jar. Using a lead pencil, mark the position of the solvent front.
6. Allow the sheet to air dry and then observe it under a short-wavelength ultraviolet lamp. Lightly mark any observable spots with a pencil and note the color of each spot.

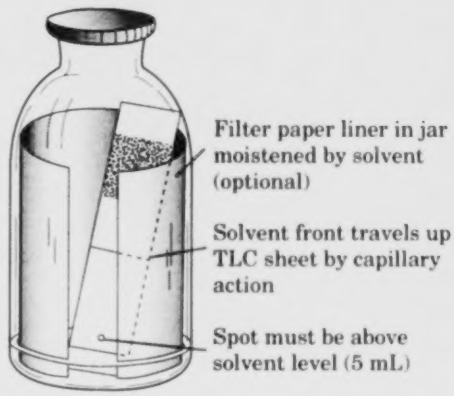

Filter paper liner in jar moistened by solvent (optional)
Solvent front travels up TLC sheet by capillary action
Spot must be above solvent level (5 mL)

Figure 3. Development jar.

7. Obtain a one-pint canning jar and place a few iodine crystals in the jar. Cap the jar and place it on a hot plate (on low heat setting), preferably in a fume hood, until purple iodine vapor is quite visible. Place the TLC sheet in a jar of iodine vapor, cap the jar, and let stand about 30 sec. Observe and record which spots become visible (darken). Remove the sheet from the jar.
8. Using a millimeter ruler, measure the distance that each spot (use center of spot for consistency) has traveled relative to the solvent front. Calculate its R_f value.

$$R_f = \frac{\text{Distance traveled by substance}}{\text{Distance traveled by solvent front}}$$

9. Obtain one-half tablet of one of the following: Anacin™, Bufferin™, B.C. Powder™, Excedrin™, Tylenol™, generic aspirin, generic acetaminophen, or an OTC analgesic of your choice. Crush the tablet on a sheet of paper with a spatula. Transfer the crushed tablet to a small test-tube and add 3 mL each of absolute ethanol and methylene chloride [*CAUTION: Avoid breathing methylene chloride. It is toxic and can have a narcotic effect in high concentrations.]*. Using a stirring rod dissolve as much of the tablet as possible. It will not completely dissolve.
10. Spot a TLC sheet with the reference solution and the unknown solution from Step 9.
11. Develop the spotted sheet in the jar as before (Steps 4 and 5).
12. Observe the sheet under ultraviolet light and mark visible spots (Step 6).
13. Observe the sheet in the iodine jar and record visible spots (Step 7).
14. Calculate R_f values for any spots (Step 8).
15. Identify the components of your unknown analgesic.
16. Thoroughly wash your hands before leaving the laboratory.

Data Analysis

1. Can ultraviolet light be used to distinguish the substances from one another?
2. Can iodine be used to distinguish the substances from one another?
3. Can the R_f value be used to distinguish one substance from another?

4. Is it important that the sheets be examined under ultraviolet light before the iodine visualization?
5. Why do some substances move along the TLC plate at a rate different from other substances?

Implications and Applications

The analysis of an unknown analgesic drug can be performed by TLC. Specific components of a developed TLC sheet can be identified by the visualization method (under ultraviolet light or in iodine vapor) and from subsequent calculations of the R_f values. Crime laboratory technicians often use TLC to determine the presence of controlled substances (*e.g.*, cocaine) in an unknown sample.

The TLC technique is often used by forensic scientists to identify pen inks. For example, the need for differentiating inks arises when people prepare fraudulent documents. A person cheating the government may back-date a record to substantiate a false tax claim. The forensic scientist can determine how many inks or pens were used to prepare a document and the year of manufacture for the inks used.

Lipstick stains on clothing or cigarettes can also give valuable information about the identity of a likely suspect. The dyes that give lipstick its color can be identified by a TLC separation and compared with those used by the friends of the victim.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Drug Identification

Major Chemical Concept

TLC is a separation technique. Specifically, substances in a mixture partition between a solid and liquid phase. A thin film of silica or alumina coated on a glass or plastic strip constitutes the solid phase. This thin film is called the stationary phase. The liquid phase is the solvent that ascends the solid layer by capillary action. The liquid phase is called the mobile phase. When a TLC sheet is spotted with a mixture of substances and placed in a solvent, the solvent (mobile phase) moves up the sheet and carries with it the various components of the spot. Because the molecules of each compound present have a different size, shape, and polarity, each compound will adhere to the stationary phase and dissolve in the solvent to a different degree. The stationary phase is typically polar and will hold polar compounds more tightly than nonpolar compounds (they will move more slowly). Less polar compounds will dissolve in the nonpolar mobile phase and move along the sheet faster. Once the flow of the mobile phase is stopped, the sheet is dried. The various spots, if not colored, can be made visible by either ultraviolet light or iodine vapor. The distance the compound moves relative to the distance the mobile phase moves is characteristic of that compound and is called the R_f value.

Level

This laboratory activity can be used in a general chemistry course.

Expected Student Background

Students should have an understanding of "like dissolves like." A polar substance is more likely to dissolve in a polar solvent rather than a nonpolar solvent. However, it will not be obvious from the structural formulas of the substances used in this activity why one substance is more polar than another.

Time

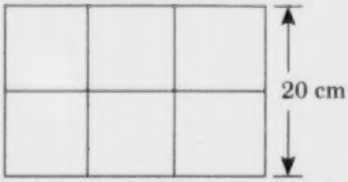
The activity may take two or three 50-min periods. During the first period students should practice spotting filter paper and TLC sheets. The developing chambers should be set up and the solvent added. A discussion of TLC could be given. During the second period, students develop the sheets containing the knowns, perform the visualization tests, and calculate the R_f values. In the third period, they develop the sheets containing the reference mixture and one or two unknowns, perform visualization tests, calculate R_f values, and identify the compounds in their unknown. If only two days can be devoted to this activity, students should work in pairs, one student obtaining the chromatogram of the knowns and reference mixture of knowns, and the other obtaining the TLC of the reference mixture and the unknown(s).

Safety

Read the *Safety Considerations* in the *Student Version*. Caution students to avoid breathing methylene chloride. It is toxic and can have a narcotic effect in high concentrations. Ethyl acetate is flammable, and its vapors can be irritating but can be minimized by keeping the developing chamber closed unless a plate needs to be inserted or removed. Iodine vapors are irritating. Students should not look at the ultraviolet light.

Materials (For 24 students working in pairs)

- 4 Small bottles (25-mL size) containing the "known" compounds in solvent (50:50 v/v methylene chloride and absolute ethanol).
- 4-Hydroxyacetanilide (acetaminophen) (1 g per 20 mL solvent)
- Caffeine (1 g per 20 mL solvent)
- Salicylamide (1 g per 20 mL solvent)
- Acetylsalicylic acid (0.5 g per 20 mL solvent)
- 1 Small bottle, 20 mL of a combined standard reference mixture of the four compounds at the same concentration. (1 g of each of the above in 20 mL of solvent. Stir to dissolve.)
- Methylene chloride, 100 mL
- Ethanol, 95%, 100 mL
- Ethyl acetate, 100 mL
- Eastman Chromatogram Sheets with Fluorescent indicator (Eastman No. 13181, box of 20 sheets). Each sheet is cut into six 10 x 6.6 cm sheets. Thus four large sheets will suffice.



- A hand-held ultraviolet lamp. Preferred: 4 watt long and short wavelength ultraviolet light. (Model Mineralight UVSL-25 available from Ultraviolet Products, Inc., 5100 Walnut Grove Avenue, San Gabriel, CA 91778 or Model UVGL-25 from Central Scientific Company, 11222 Melrose Avenue, Franklin Park, IL 60131-1364)
- Thin-wall, open-end capillary tubing (1 mm) for micropipets; alternatively, use toothpicks
- Filter paper, 12 squares for liners
- 24 Wide mouth, clear screw cap jars (Mason jars will work), 16 oz, or 600-mL beaker with aluminum foil cover also work well
- Iodine, several crystals

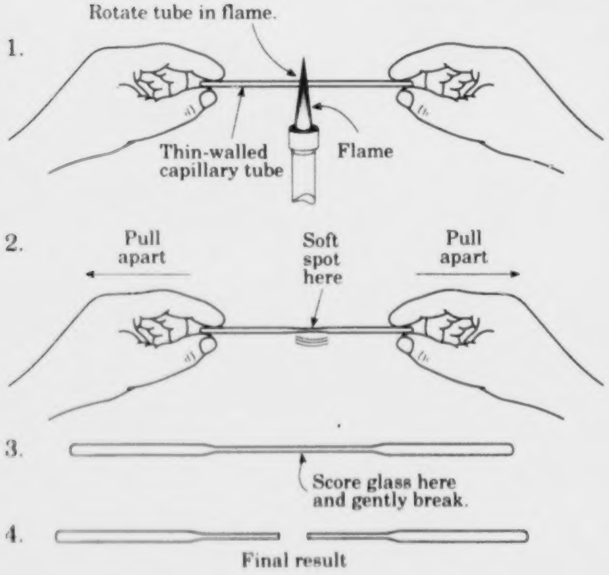


Figure 4. Preparation of micropipets.

Advance Preparation

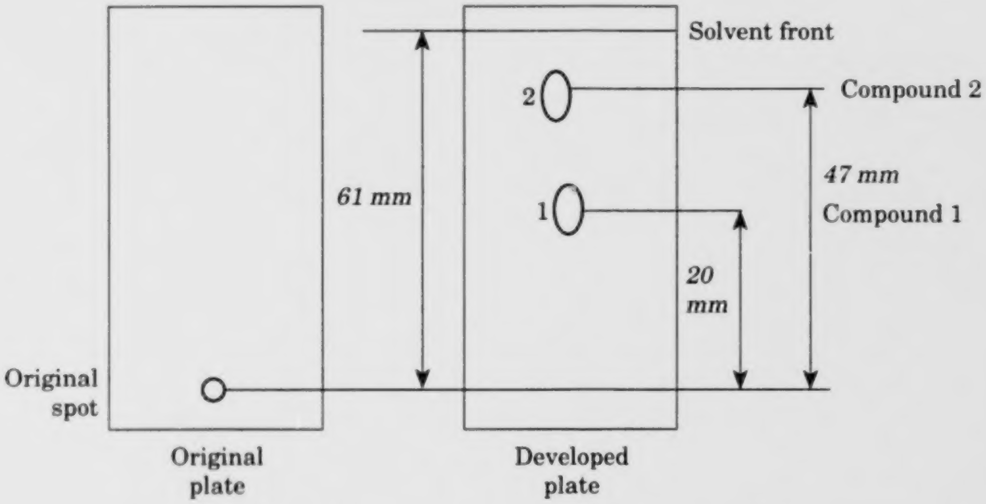
Prepare the solutions of the knowns before the laboratory period. Spot the TLC in one area of the laboratory. Have students come to a table of knowns rather than taking the knowns to their individual desks. Keep development chambers at individual desks. Place the ultraviolet lamp in a darkened hood, darkened area of the laboratory room, or in a large upside-down cardboard box with appropriate holes cut for viewing.

Prepare about 10 micropipets as shown in Figure 4.

Pre-Laboratory Discussion

1. Give a brief introduction to the TLC techniques (see *Major Chemical Concept*).
2. Instruct students on importance of small spots. If spots are too large, tailing and poor separation will occur.
3. Explain why the spotted mixture should be above the solvent level. (If it is below, it will dissolve in the solvent and not separate.)

4. Remind students not to move the jar during the development time to avoid splashing solvent on the plate.
5. Explain to students how to calculate R_f values. Tell them to get their best estimate for the center of each developed spot.



$$R_f(\text{Compound 1}) = \frac{20}{61} = 0.33 \qquad R_f(\text{Compound 2}) = \frac{47}{61} = 0.77$$

Figure 5. Calculation of R_f values from chromatograms.

Teacher-Student Interaction

Walk around laboratory and ask students if they understand what is happening. Discuss how to calculate R_f values. Caution students about inhaling solvent vapor.

Anticipated Student Results

Typical experimental results are:

$$R_f = \frac{\text{Distance traveled by substance}}{\text{Distance traveled by solvent front}}$$

Knowns

$$R_{f\,AC} = \frac{3.2\text{ cm}}{7.4\text{ cm}} = 0.43$$

$$R_{f\,ASP} = \frac{0.7\text{ cm}}{7.4\text{ cm}} = 0.09$$

$$R_{f\,CF} = \frac{2.0\text{ cm}}{7.4\text{ cm}} = 0.27$$

$$R_{f\,SAL} = \frac{5.4\text{ cm}}{7.4\text{ cm}} = 0.73$$

Unknowns

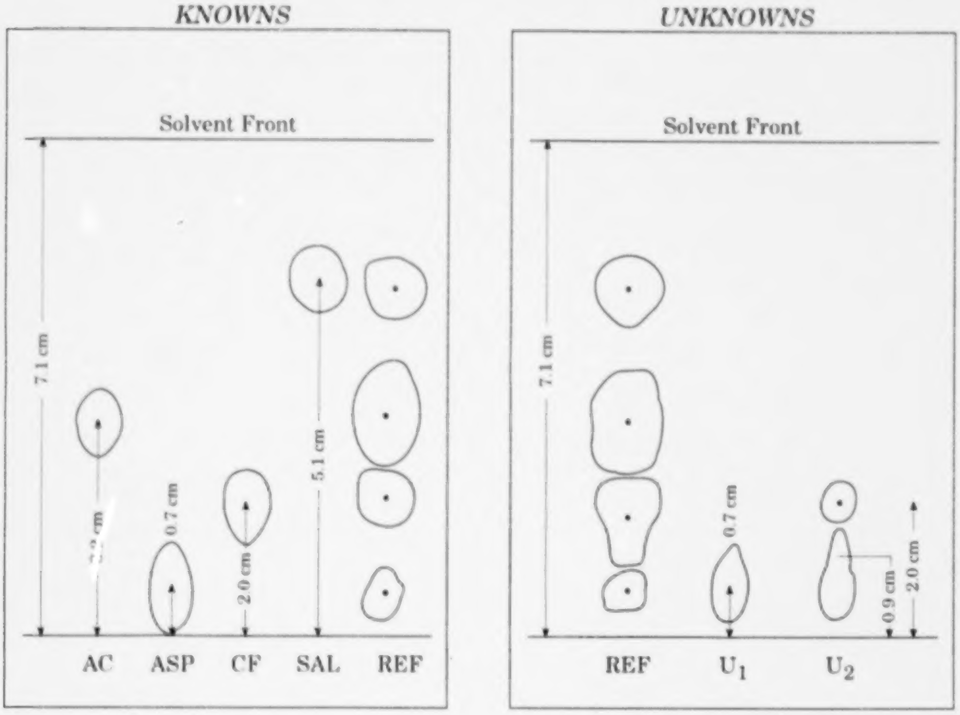
$$R_f, U_1 = \frac{0.7\ \text{cm}}{7.1\ \text{cm}} = 0.10\ \text{(Aspirin)}$$

$$R_f, U_2 = \frac{0.9\ \text{cm}}{7.1\ \text{cm}} = 0.13\ \text{(Aspirin)}$$

$$R_f, U_2' = \frac{2.0\ \text{cm}}{7.1\ \text{cm}} = 0.28\ \text{(Caffeine)}$$

The SAL spots fluoresce bright blue and the AC and SAL spots darken in iodine.

Figure 6. Typical experimental results. (NOTE: The reference spots may not completely separate.)



Post-Laboratory Discussion

Review the results of the activity. Have students come to the conclusion that an analgesic drug can be identified through TLC.

Suggestions for Other Laboratory Activities

Design TLC and paper chromatography (see *Demonstration 3* in the *Separations* module and *Demonstration 3* in the *Solutions* module) activities to separate inks or lipsticks.

Answers to Data Analysis

1. Salicylamide exhibits a bright-blue fluorescence.

2. Salicylamide and acetaminophen produce dark spots. Caffeine produces a light spot. Aspirin does not produce a spot.
3. Yes. The approximate order of migration is salicylamide, followed by acetaminophen, caffeine, then aspirin.
4. Yes. The iodine permanently darkens some of the spots.
5. The differences in the rate of movement of substances depend upon solubility of the substance and adsorption properties of the backing on the plate. Because the solvent is typically nonpolar and the backing is strongly polar, the backing holds a polar substance more tightly than a nonpolar substance. These polar substances move considerably more slowly than nonpolar substances in the nonpolar solvent.

Assessing Laboratory Learning

1. List the steps in the determination of the number of components in a mixture by TLC. *[Spot the plate, develop the chromatogram, visualize the spots, calculate R_f values, compare with suspected knowns.]*
2. How is an R_f value determined? *[R_f is the distance the substance travels divided by the distance the solvent travels.]*
3. Two substances have R_f values of 0.3 and 0.5, respectively. Which substance is carried farther by a polar solvent? Which substance is less polar? *[Substance with $R_f = 0.5$ is the polar substance and is carried better by the polar solvent. Substance with $R_f = 0.3$ is less polar.]*
4. Name two ways of visualization of spots. *[Ultraviolet light and iodine vapor. Discuss with the students other possibilities for visualization. Lead them to think about color reactions, where the spots can be developed by spraying the TLC plate with reagents that react with the samples to give a color or a visible spot. For example, ninhydrin sprayed on hydrolyzed protein samples yields a purple color and conc. sulfuric acid dehydrates most organic compounds to yield yellow to brown (carbon) spots (see Demonstration 3).]*
5. Identify the stationary and mobile phases in TLC. *[Solid adsorbent and solvent, respectively.]*
6. Using the following chromatogram, decide which substances are identical? Which mixtures are identical? *[Identical substances: 1a, 2a, and 4a; 1b, 3b, and 4b; 1c and 4c. Identical mixtures: 1 and 4.]*

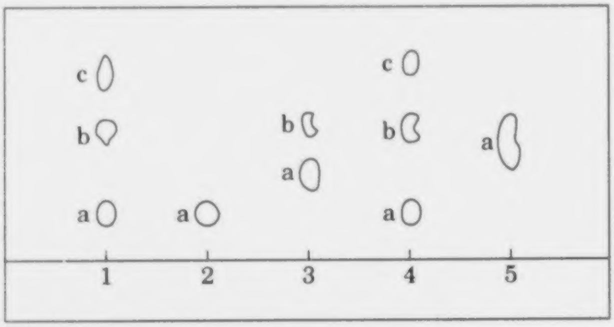


Figure 7. Chromatogram of unknowns.

DEMONSTRATIONS

CAUTION: Use appropriate safety guidelines in performing demonstrations. Only brief procedural steps are described here. Some of these demonstrations can be used as student activities.

Demonstration 1: Density of Glass

The analysis of shattered glass is very important in burglary and automobile accident cases. In addition to the glass particles left at the crime scene, some glass particles are also found on shoes or clothing of the suspect or on some parts of the car. If particles from the scene compare with those found on the suspect, the prosecution's evidence is strengthened.

Glass is a noncrystalline material of widely varied composition and properties. It contains silicon dioxide (sand), metallic oxides or carbonates, and other trace elements. The properties depend on the method of production, the annealing time and temperature, and the composition. The physical properties of glass vary sufficiently that they can be used to compare two samples of glass with each other. Glass gives a different appearance when viewed under ordinary light, ultraviolet light, and polarized light. Glasses also vary in density and index of refraction (see *Demonstration 2*). In this activity you will view two glass samples under the light described above and determine the density of a glass sample from its mass and volume (by water displacement).

Part A. Appearance of Glass Samples

Materials

2 Different glass bead samples
Ultraviolet lamp
Microscope
Polarized film set
Magnifying glass

Safety

Do not look directly at the ultraviolet lamp. Care must be taken when handling glass fragments because of sharp edges.

Procedure

1. Obtain a sample of each type of glass.
2. Observe the glass samples under a direct light using a magnifying glass.
3. Observe the glass samples under ultraviolet light using a magnifying glass.
4. Observe each glass sample under the microscope between two polarized films. One film should be positioned permanently while the other one is rotated 90°. As you rotate the film, more and more light is blocked out.
5. Compare the two glass samples under the three kinds of lighting. Are they distinguishable?

Part B. Density of Glass Samples

Materials

2 Different glass bead samples
Balance
Graduated cylinder, 10-mL
Water, 100 mL

Procedure

1. Add 2-3 mL of water to the graduated cylinder. Read the volume to the nearest 0.01 mL. Determine the mass. Record both the volume and mass.
2. Add enough glass beads from one sample to the cylinder to increase the volume by about 5 mL. The additional glass beads should be submerged. Read the new volume to the nearest 0.01 mL and record. Determine the mass of this new combination and record.
3. Determine the density of this glass sample and record results.
4. In order to be sure your density is reliable, add a few more beads to this same cylinder. Record the final volume and determine the new mass.
5. Determine the density of this second trial by subtracting this final volume from the initial volume and by subtracting the final mass from the initial mass. Record results. Take an average of the two densities and record this average on the data sheet.
6. Repeat Steps 1-5 for the other glass sample.

Demonstration 2: Refractive Index of Glass

Refractive index is a measure of the bending of light as it passes from air into a solid or liquid. Determination of the refractive index of glass provides information about the common origin (or lack thereof) of two glass samples.

In the immersion method a glass sample is added to a pure liquid or liquid mixture of known refractive index. If the glass and liquid have different refractive indices, a colored boundary can be seen with the unaided eye. If they have the same index of refraction, the boundary will disappear and the specimen will be practically invisible.

Materials

Several fragments of Pyrex™ glass
Several fragments of common (flint) glass
Baby oil or vegetable oil
Test-tubes

Safety

Sharp glass may cause cuts and should be handled with care.

Procedure

1. Fill three test-tubes about half-full of oil.
2. Put some of the Pyrex™ fragments in one test-tube, some common glass fragments in another, and a mixture of Pyrex™ and common fragments in the third.
3. Stopper the three test-tubes. Observe.
4. The Pyrex™ glass will be nearly invisible when covered with the oil, while the flint glass will remain visible. The Pyrex™ glass has an index of refraction (1.47) that nearly matches the index of refraction of the oil, whereas flint glass has an index of refraction of 1.60.
5. Discussion. Many crime laboratories have a standard set of liquids of varying refractive index over a wide range and in small increments (typically 0.05). These so-called Cargille liquids allow the forensic specialist to determine the refractive index of transparent samples to an uncertainty of ±0.05 by the immersion method.

Demonstration 3: Analysis of Fingerprints

Fingerprints are the most reliable means of identifying suspects. No two human fingerprints are exactly alike, and fingerprints do not change naturally. Fingerprints are classified into three main types: loop, arch, and whorl (see Figure 8). There is no set number of *points* of similarity used by experts when comparing fingerprints for identification. However, many latent print examiners often use seven *points* as a minimum.

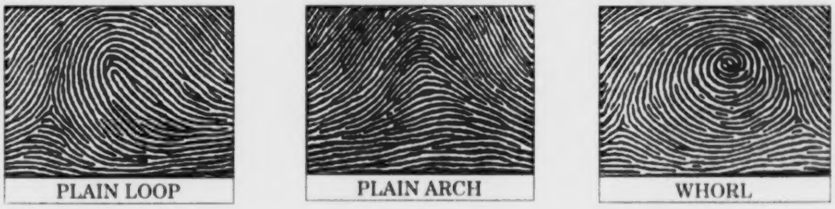

PLAIN LOOP
PLAIN ARCH
WHORL

Figure 8. Types of fingerprints.

Part A. Obtaining a Fingerprint

Materials

Black ink stamp pad
Tissue paper
4 x 4 cm Card (cut from a 3 x 5 inch file card)
Tweezers

Safety

Wash hands thoroughly to remove the black ink.

Procedure

1. Handle the card only on the edges.
2. Place your right thumb on the black ink pad and then place your thumb print in the middle of the card.
3. Examine the print and identify it by main type.
4. Compare with other students in the class who have the same main type to determine if there are distinguishing features in the thumb prints.

Part B. Dusting for and Lifting Prints from a Smooth, Nonporous Surface

Materials

Dusting brush (one for each color of powder)
Dusting powders (aluminum and carbon black).
2 Beakers, 150-mL
Newspaper
2-inch wide Cellophane tape
Index card
Magnifying glass

Safety

Take care not to scatter dusting powders. Some people are sensitive to the airborne particulates.

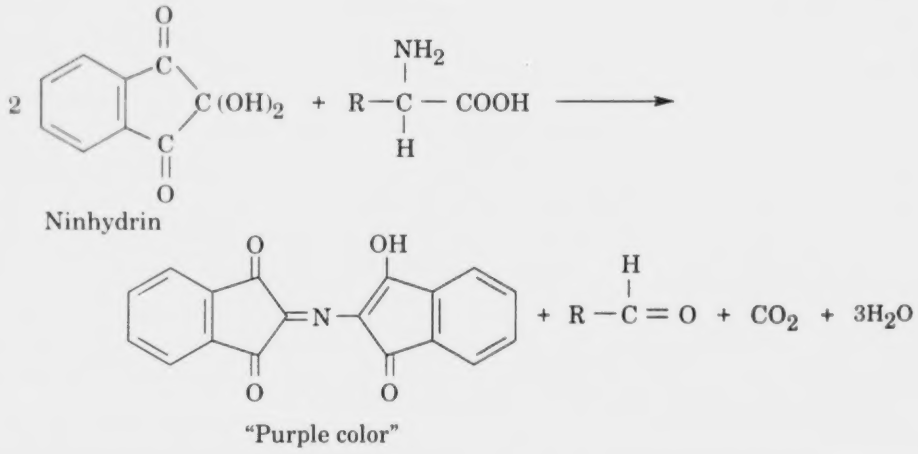
Procedure

1. Grab a 150-mL beaker so that your thumb print is left on the beaker.
2. Obtain a brush for dusting the print. Make sure it is clean and the bristles are separated from each other.

3. Place a small amount of the dusting powder in a labeled beaker. Dip the brush in the powder and lightly dust the area containing the print. After the entire print is developed, remove the excess powder by gently brushing it away. Be careful not to destroy the print with too hard a brush stroke.
4. To lift the print from the 150-mL beaker to the index card, unroll 9 cm of tape. Bend the tape strip in the form of a U so that the sticky side is facing the beaker. Place the point of the fold directly on the print. Gently place the rest of the stripe onto the beaker. The print can be removed by pulling up on the roll end of the tape and then placing it on the fingerprint card in the same manner as the tape was placed over the latent print. Make sure the tape is secure. Cut off the excess tape.
5. Observe the print under the magnifying glass and compare it with your right thumb print from *Part A*.

Part C. Using Ninhydrin to Develop a Print on Paper

Ninhydrin reacts with amino acids in the perspiration on a fingerprint to form a purple compound. The reaction of ninhydrin with an amino acid may be represented as follows:



The purple-colored substance is formed by the reaction of some of the ninhydrin with its reduction product, hydrindantin, and ammonia, which is formed as a reaction intermediate.

Safety

Wear plastic gloves when handling ninhydrin since it will stain skin. Ethanol is volatile and flammable. Keep the solution away from open flames.

Materials

4" x 5" Sheet of white paper containing your right thumb print
Ninhydrin solution (0.3 g ninhydrin in 100 mL ethanol)
Forceps
Plastic gloves
Brush or cotton wads
Magnifying glass
Concentrated ammonia or steam iron

Procedure

1. Tape the top of the exhibit (white sheet of paper containing your right thumb print) to a paper towel. Do the following in a fume hood or in a well ventilated area. The ethanol used in preparing the ninhydrin solution is volatile and flammable. Keep this solution away from open flames. Wear plastic gloves when working with the ninhydrin solution as it will react with the amino acids in your hand and turn them blue to purple!
2. Dip the tip of the brush into the ninhydrin solution and carefully dab this liquid over the fingerprint area. Do not use too much pressure since that will destroy the print. Cotton wads held with tweezers can also be used to dab the liquid onto the fingerprint area.
3. Allow the paper to dry. It may take 24 hrs to develop. Observe the print under a magnifying glass and compare with the fingerprint obtained above.
4. If the print does not develop, expose the paper to the fumes from ammonia by opening a bottle of concentrated ammonia in the fume hood and holding the paper with the print over the opening of the bottle. Alternatively, a steam iron may be used.

Demonstration 4: Lipstick Fluorescence

Many substances contain molecules that absorb radiation in the ultraviolet portion of the spectrum and because of certain intramolecular phenomena, emit radiation in the visible region of the spectrum. This phenomenon is called fluorescence (see *Photochemistry* module). In this activity you will examine the fluorescence of lipstick. These observations suggest why makeup may appear different in a disco, or under a street light, as compared to inside a room.

Materials

Lipstick samples
Filter paper
Ultraviolet lamp

Safety

Ultraviolet light can damage eyes. Do not look directly at the ultraviolet light.

Procedure

1. Obtain the several lipstick samples to be used in this demonstration. Record the color and manufacturer for each type, then describe the color.
2. Use a sheet of filter paper. Place a smear of each kind of lipstick onto the paper, using a mark about one-half inch long. Write the brand or other identification next to the smear for identification.
3. Expose the filter paper containing the lipstick stains to an ultraviolet lamp in a dark room. Observe which of the lipstick samples fluoresce under the light and circle those samples.

Demonstration 5: Examination of Hair

Hair is a common form of evidence in many homicide and sexual assault cases. Hair from any part of the body exhibits a range of characteristics such as color, length, and diameter. The parts of a hair that are easily seen by use of a microscope under magnification are the medulla and cortex. It is very difficult to see the hair cuticle. Figure 9 illustrates the parts of a hair and the various types of hair.

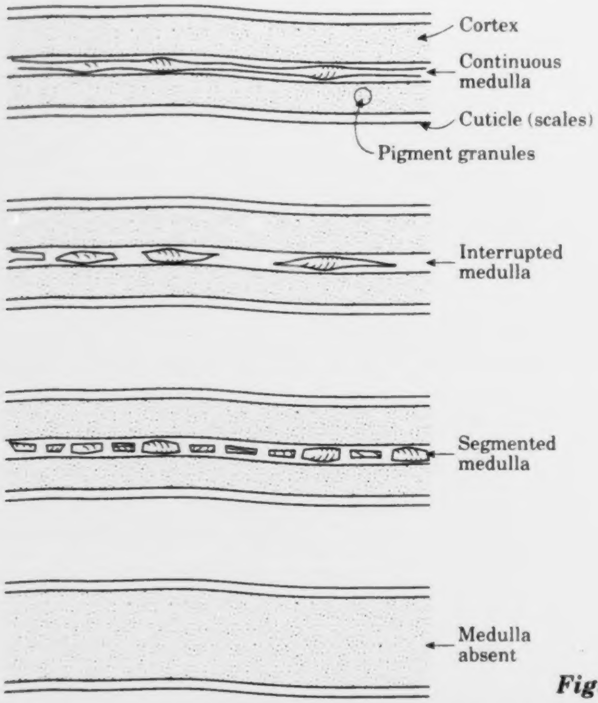


Figure 9. Types of hair.

Many animal hairs are easily distinguished from human hairs by the size and shape of their medullae and the patterns of their cuticle or scale structures (see Figure 10). Synthetic fibers have no medulla or scale pattern and are therefore readily distinguishable from animal hair.

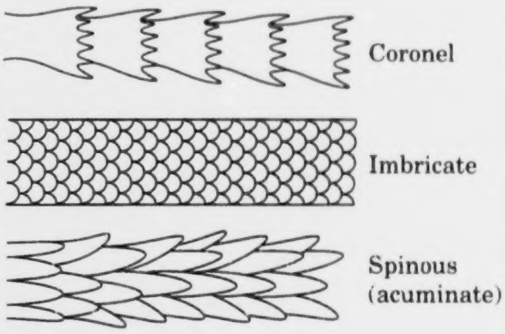


Figure 10. Types of animal hair.

Materials

Microscope slides
Compound microscope (100X is a good magnification)
Tissue paper
Tweezers
Hair sample (yours, animal)
Fiber sample
Glycerol (glycerin)
Safety:
Glycerol (glycerin) should not be ingested.

Procedure

1. Obtain a strand of human hair and place it on a microscope slide.
2. Place a small drop of glycerol on the hair in order to hold it in place, and put a cover slip over it.
3. Place the slide on the stage of the compound microscope, clip in place, and adjust the magnification at 100X.
4. Locate the root end of the hair, if it has one. If the hair has been forcibly pulled out, you will see a bulb-shaped enlargement. This is the root.

5. Make a sketch of what you see.
6. Scan along the length of the hair body. Is the medulla (center) fragmented (present in isolated spots), interrupted (long columns with open spaces now and then), or continuous (unbroken column)? Make a sketch of the medulla you observe from the hair sample.
7. Note the color, diameter, and pigmentation of the hair.
8. Examine the tip of the hair. This can be done by observing a gradual tapering of the hair. If the hair has been recently cut, you will see a square tip where the hair ends abruptly. Normally, hair tapers to a fine point as it grows. If hair has split-ends, it is normally due to artificial waving or bleaching, although repeated brushing may also produce this effect.
9. Repeat Steps 1-8 for the sample of animal hair. Note any similarities and differences with the human hair.
10. Try to obtain various colors of hair from other persons in the class. Make comparisons about similarities and differences.
11. Obtain a fiber strand (cotton, nylon, silk, wool, Dacron, linen, rayon) and observe the color. If present, the color is due to a dye or stain. Prepare a microscope slide of the fiber and try to determine if the dye penetrates the fiber, or is found only on the surface.
12. Examine other fiber characteristics such as diameter, whether the surface is rough or smooth, whether the fiber is twisted or straight, whether it is continuous, or segmented, whether it is round, flat, oval, or has some other shape.
13. Compare and contrast human hair, animal hair, and fiber.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. What are examples of physical evidence? *[Body fluids, hair, fingerprints, handwriting, tool marks, firearms, fibers, soil, inks, documents,* etc.*]*
2. Why is examination of physical evidence undertaken? *[For identification and comparison.]*
3. What is the purpose of identification? *[To determine a substance's physical or chemical identity with the certainty permitted by the analytical technique used.]*
4. What is the purpose of comparison? *[Comparison subjects the suspect and control specimens to the same tests and examinations to determine if a common origin exists.]*
5. Name some analytical techniques used by the forensic scientist. *[Electrophoresis, chromatography (gas, thin layer, high pressure liquid), spectroscopy (infrared, ultraviolet), neutron activation analysis, and atomic absorption spectroscopy.]*

Counterintuitive Examples and Discrepant Events

1. Appearances are deceiving.
2. Not all criminals look the part.
3. Things that look the same on the surface are different inside (*e.g.*, antiques versus reproductions).

Metaphors and Analogies

1. Forensic chemistry is like a zipper—everything must fit together.
2. Forensic chemistry is like the spokes on a wheel—to form a strong case, each spoke has to fit in the correct place.

Language of Chemistry

TIPS FOR THE TEACHER

1. A full-service crime laboratory consists of specific units. These include (in addition to the unit's function):
   a. **Physical Science Unit**: Applies principles of chemistry, physics, and geology (*e.g.*, identification of glass, soil samples, or tire marks) to the identification and comparison of crime-scene evidence.
   b. **Biology Unit**: Examines blood, body fluids, hair, fibers, and botanical specimens.
   c. **Firearms Unit**: Examines firearms, bullets, cartridge cases, shotgun shells, tool marks, latent prints, and ammunition of all types.
   d. **Document Examination Unit**: Examines handwriting and typewriting on questioned documents; analyzes paper and ink, indented writings, obliterations, erasures, and burned or charred documents.
   e. **Toxicology Unit**: Examines body fluids and organs for drugs and poisons.
   f. Other units include the **Identification Unit** (photography, fingerprint, polygraph, and voice-print analysis), and Evidence Collection Unit.
2. The **Evidence Collection Unit** dispatches trained personnel to the crime scene to retrieve evidence for laboratory examination. Physical evidence can be anything from massive objects to microscopic traces. The presence of many items of evidence is obvious, but some can only be detected by close laboratory scrutiny. Many examples of physical evidence were described above.
3. Forensic science is the application of science to criminal and civil laws.
4. Chemistry, biology, physics, and geology are useful for determining evidential value of crime scene and related evidence.
5. Forensic scientists may be called to testify in civil cases (*e.g.*, water quality or product liability).
6. The microscope is the most important tool in some crime laboratories. TLC is an important technique and GC is an important instrument.
7. Forensic scientists often deal with small amounts of the evidential sample, often necessitating, as the first choice, examination by a nondestructive laboratory test.
8. Samples examined by forensic chemists are usually impure. Tests will show the presence of "something" in a lot of "garbage."
9. Forensic science laboratories are seldom on the forefront of technology in chemistry (or science). Attorneys and judges feel comfortable with what has already been accepted in the courts. On occasion, evidence will be accepted if it provides information that cannot be obtained otherwise (*e.g.*, DNA profiling).

10. Confiscated street drugs may require extraction, isolation, and spectral analysis for identification. Extraction of a suspected compound from a mixture is often pH dependent (many of these compounds contain basic groups), dependent on the solubility of the suspected compound in the extraction solvent, and the resulting crystalline form depends on whether the substance is precipitated in neutral, acid, or base form. This may also be true of some pharmaceutical samples.

Common Student Misconceptions

1. **"Forensic chemistry can solve all crimes."**

   Forensic chemistry is only one of the sciences important in crime solving. The principles and techniques of biology, geology, and physics are applied to the many types of evidence. Mathematics and psychology are also important areas.

2. **"Crimes can be solved easily."**

   Despite the fact that many crimes as portrayed on television and in the movies are solved within 1-2 hrs, most crimes require a team effort involving deductive reasoning and sophisticated scientific techniques over a period of time. Some crimes are never solved.

3. **"Perfect fingerprints can be taken off anything."**

   Generally, smooth surfaces (glass, table tops, *etc.*) will yield good fingerprints; a rough surface (stone wall) will not. The quality of a fingerprint is also determined by the amount of skin oil.

4. **"Identical twins have the same fingerprints."**

   Fingerprints are individualized. In addition, other types of physical evidence that can be individualized include jigsaw matches, footwear and tire tread prints, striations present in tool marks, and ballistic evidence.

History: On the Human Side

1. **Alphonse Bertillon** (1879) developed a systematic procedure of taking a series of body measurements as a means of distinguishing one individual from another.
2. **Sherlock Holmes**, in Sir Arthur Conan Doyle's *A Study in Scarlet* (1877), described scientific methods of detection years before they were actually discovered and implemented. In the novel mentioned here, Holmes describes a chemical test for blood.
3. **Francis Galton** (1892) published a book describing the principles of the present system of fingerprint identification.
4. **Leone Lattes** (1915) devised a procedure for determining the blood group of a dried bloodstain. The procedure is still utilized today.
5. **Calvin Goddard** helped establish the comparison microscope as the indispensable tool of the modern firearms examiner.
6. **Albert Osborn** (1910) developed the principles of document examination.
7. **Edmond Locard** (1910) established the first workable crime laboratory in which the principles of chemistry, physics, mineralogy, and biology were utilized. He enunciated the creed of the forensic scientist when he said every criminal *carries something to and takes something from the crime scene.*
8. In 1932, the FBI organized a national laboratory that offered forensic services to law enforcement agencies throughout the country.

9. In 1948, the first school of criminology was formed at the University of California at Berkeley.
10. The Central Research Establishment in England was formed in 1966 and dedicated to performing basic research in forensic science (development of new forensic procedures, gathering statistical data, and collecting and disseminating vital information).

HUMOR: ON THE FUN SIDE

1. a. Silverstone, L. (1981, January). Queezy, *MAD*, *220*, p. 43. E. C. Publications, Inc., 485 Madison Avenue, New York, NY 10022. A satire on a popular television show, "Quincy," about a medical examiner portrayed by Jack Klugman.
   b. *Murder in a Bookstore* (Treat, 1981). Used by permission of the publisher.

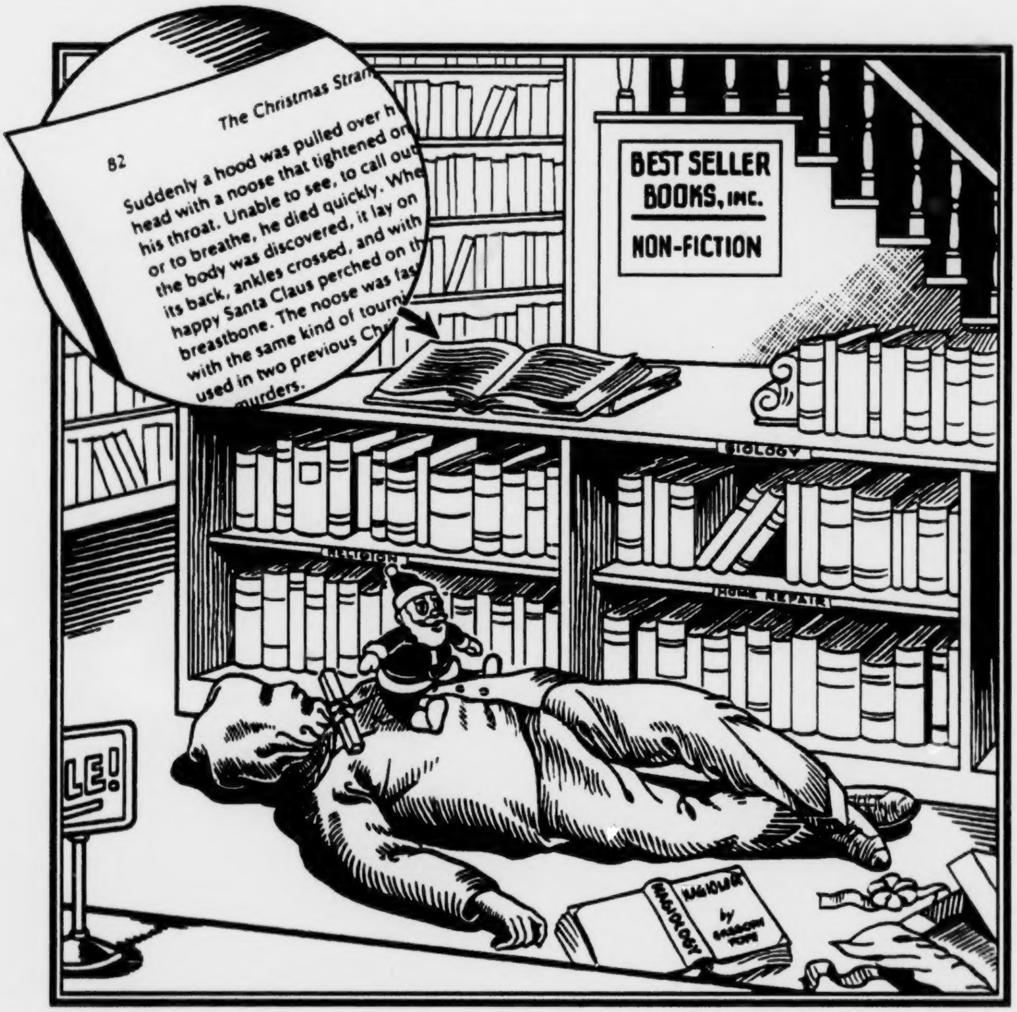

The Christmas Stra
82
Suddenly a hood was pulled over h
head with a noose that tightened or
his throat. Unable to see, to call out
or to breathe, he died quickly. Whe
the body was discovered, it lay on
its back, ankles crossed, and with
happy Santa Claus perched on th
breastbone. The noose was fas
with the same kind of tourni
used in two previous Ch
murders.
BEST SELLER BOOKS, INC.
NON-FICTION
BIOLOGY
RELIGION
HOME REPAIR
LE!
HAGIOLOGY by GREGORY POPE

Figure 11. Murder in a bookstore.

On December 23rd the body of Quintus Tertius, a bibliophile, was found as shown in the basement of the Boswell Bookstore. Page 82 of *The Christmas Strangler*, by Elden Hack, lay open on a counter. Mr. Tertius, a regular customer, often rummaged in the stacks of books in the basement.

Eppis Pepys and his wife, Alice Pepys, were proprietors of the Boswell Bookstore. Each of them admitted having gone down to the basement within a half hour of the probable time of the murder.

E. Pepys said, "I went down to get a copy of Descartes' *Principles of Philosophy*. I saw no one in the basement."

A. Pepys said, "I went down to get a copy of Spinoza's *Ethics*. I saw no one in the basement."

From these facts and from an examination of the scene, can you tell who killed Quintus Tertius, and why?

Questions

1. Did Tertius commit suicide?
2. Is it likely that the murderer entered and left the bookstore without being noticed?
3. Do you think Tertius was reading *The Christmas Strangler* when he was accosted?
4. Did the murder method require preparation?
5. Do you think the killer brought his murder equipment with him?
6. Did Eppis Pepys have a motive for killing Tertius?
7. Did Alice Pepys have a motive for killing Tertius?
8. Do you think that the killer brought *The Christmas Strangler* with him?
9. Do you think that Tertius was engrossed in reading at the time of his murder?
10. Can you figure out a probable motive for this murder?
11. Who do you think killed Tertius?

Answers

1. No. You can't strangle yourself with a tourniquet. Don't try it!
2. Yes. December 23rd was at the height of the Christmas rush, when bookstores are crowded. Any bookseller can expand on the ordeal.
3. No. This was a nonfiction area frequented more by bibliophiles than mystery readers, and *Hagiology*, by Gregory Pope, lay open near the victim's hand, suggesting that he was reading this book when attacked by the murderer.
4. Yes. This is obvious from the presence of the tourniquet, the hood, and the gloating little Santa Claus, which are not objects ordinarily taken on a trip to a bookstore.
5. Yes. The opened package next to the body indicates how the murderer brought his equipment here.
6. No. You don't kill your customers. This is a rule that all booksellers follow faithfully.
7. No, for the reasons cited in (6).
8. Yes. This is a nonfiction area, where mystery novels would feel unwanted.

9. Yes. Otherwise it would have been difficult to throw a hood over him without leaving evidence of a fight.
10. Yes, publicity for the book.
11. Elden Hack, in order to get publicity for his book, which it got. And so did he.

c. CLUE™ Logic Problem

Logic problems are interesting and challenging forms of entertainment for many people. The challenge comes about because of the deductive reasoning processes that must be invoked. This example is developed around the game CLUE™, a copyrighted game produced by Parker Brothers. This version was developed and used by permission of Keith Berry.

Setting: It was a very curious weekend when six victims (Kelly, Lynn, Robin, Leslie, Dana, and Chris) were invited by the owner of a great mansion (Colonel Mustard) and five of his friends (Miss Scarlet, Professor Plum, Mrs. Peacock, Mrs. White, and Mr. Green) to a grand party. Unfortunately, by the time the Inspector was called to the scene, all of the victims had died under strange circumstances, none before noon and none later than 10:00 P.M. on that Saturday.

Procedure: Using the data statements below, you are to help the inspector determine who was killed in each murder, the weapon that was used by each, the room in which the crime occurred, the time at which each murder took place, the name of the victim for each of the murders, and the sex of each victim. All victims died in different rooms, at different times and from different weapons.

Data

1. Four victims were males, none of whom were killed before 2:00 P.M., shot, or found in the lounge, kitchen or conservatory.
2. Each murder occurred while the great grandfather clock was striking an even number. The clock sounded only on the hour.
3. Leslie and his twin sister arrived at 6:00 P.M., being greeted by their very good friend, Miss Scarlet, with whom they talked for 20 min.
4. The woman who used the candlestick killed a female in the conservatory.
5. Mrs. Peacock was in the library all afternoon, but was not strong enough to use a wrench.
6. Robin had once been married to Professor Plum and knew only him and her killer from among all those in the house when she got there early in the morning.
7. The person who fired the revolver in the lounge killed one of the twins after a person had already been stabbed to death.
8. The person who used the wrench used it at 4:00 P.M., just after the rope had been used and just before the knife was used.
9. All weapons were found in the room where they were used; none was found in the kitchen or dining room.
10. Kelly did not die before 5:00 P.M.
11. Professor Plum's victim was found in the study but had not been there when Colonel Mustard had gone in at 9:00 P.M.
12. The ballroom was being remodelled so no one could get into it.

13. Dana took a brief walk at 7:00 P.M., but the other female had been dead for at least 6 hrs by that time.
14. The man who knifed Kelly loved to play billiards just before his 7:30 P.M. dinner, which always lasted one hour.
15. The twin that was the last of all the victims to die was struck with the lead pipe by a man.
16. Lynn was strangled at 2:00 P.M., 2 hrs after Miss Scarlet had killed and 2 hours before the person died in the hall.
17. Mrs. White, who left the house for the last time at 4:30 P.M., killed neither Kelly nor a female, and did not go into the study, the billiard room, the library or the conservatory all that day.
18. Professor Plum's victim died 2 hrs after his sister.
19. Mr. Green, who did not use either the wrench or lead pipe, did not get to the house before 6:00 P.M., and had never been in the library.

Suggestions for Proceeding and Report

Use the data table to help organize your data. Insert some sort of a mark to indicate which combinations of factors are not possible, and a different mark to indicate which are certain events. For example, use a circle to mark those that did happen, and an "X" to mark those that didn't.

MURDERER	WEAPON						ROOM									TIME						VICTIM					
	Pipe	Rope	Wrench	Candlestick	Knife	Revolver	Study	Hall	Lounge	Dining Room	Kitchen	Ballroom	Conservatory	Billiard Room	Library	12	2	4	6	8	10	Kelly	Lynn	Robin	Leslie	Dana	Chris
Col. Mustard																											
Miss Scarlet																											
Prof. Plum																											
Mrs. Peacock																											
Mrs. White																											
Mr. Green																											
Kelly																											
Lynn																											
Robin																											
Leslie																											
Dana																											
Chris																											
12																											
2																									M	F	
4																											
6																									SEX		
8																											
10																											
Study																											
Hall																											
Lounge																											
Dining Room																											
Kitchen																											
Ballroom																											
Conservatory																											
Billiard Room																											
Library																											

Turn in your data table, noting what each type of mark represents.

Turn in your conclusions as to: murderer, room, time, weapon, victim, and victim's sex. See *Appendix* to make extra copies of data table.

Answers to Clue™ Logic Problem

	1	2	3	4	5	6
Murderer	Scarlet	Plum	Peacock	White	Green	Mustard
Room	Conserv.	Study	Library	Hall	Lounge	Billiard
Time	12:00	10:00	2:00	4:00	8:00	6:00
Weapon	Candle	Pipe	Rope	Wrench	Revolver	Knife
Victim	Robin	Leslie	Lynn	Chris	Dana	Kelly
Sex	Female	Male	Male	Male	Female	Male

2. Word Search (see *Appendix* for master copy)

B W Y Q P I K V E B C V T K J W T
Y P H G X X W P T ~~A N A L Y S I S~~
P W W L O C J X M U U D G C H L K
O W G Z M L F E H J Q O S N E M M
C ~~T L C~~ C H O P I Y L P P I D C Y
S L M B S X A C S O P V G U N H D
O X U N C R T M I F M N L Q A M E
R X N J G M R B N X P C S I I R C
T B E Y C A Z L A U O S C K Z Z W
C X L P E X T T O T S T D K A U F
E O J R H C E I E L X A T Q M C U
P E I J L D S J G Y L J P Y A Y O
S F Z ~~Y H P A R G O T A M O R H C~~

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Analysis technique used to separate mixtures into their component parts.
2. Another name for a lie detector.
3. Carrier of genetic information used by forensic chemists to match samples of body fluids to suspects (Abbrev.).
4. Separation technique using silica-coated glass or plastic plates (Abbrev.).
5. Technique used by forensic chemists to identify compounds by their interaction with radiation.
6. Forensic unit dealing with poisons or drugs.
7. Forensic unit dealing with blood, body fluids, hair, fibers, and botanical specimens.
8. Process of breaking down whole information available into its components.
9. Forensic unit that examines bullets, cartridge cases, and ammunition.
10. TV forensic chemist played by Jack Klugman.

Answers: 1. CHROMATOGRAPHY 2. POLYGRAPH 3. DNA 4. TLC 5. SPECTROSCOPY 6. TOXICOLOGY 7. BIOLOGY 8. ANALYSIS 9. FIREARMS 10. QUINCY

3. See cartoons at end of module.

MEDIA

1. Videotapes of "Demonstrations of Forensic Techniques," prepared by Everett Nienhouse, Vikas Productions, 8 Circle Lane, West Lafayette, IN 47906; (317) 743-3053; (317) 494-0706; $89.95 each; $600 for the set.

Vol. 1	Basic Laboratory Measurements and an Introduction to Forensic Pathology.
Vol. 2	Forensic Microscopy: The Compound and Stereomicroscope
Vol. 3	Firearms Evidence Examination
Vol. 4	Analysis of Corrosive Materials; Acid/Base Concepts Encountered in Forensic Science
Vol. 5	Analysis and Identification of Drugs
Vol. 6	Gas Chromatography: The Analysis of Arson Debris
Vol. 7	Forensic Serology: The Analysis of Blood

2. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   Spec20, by Ralph Gable and James McCormick. Vol. IV, No. 1, for IBM PS/2 PC-compatible computers.

3. Videodisc published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   "Mercury Determination Using a Spectrophotometer–Accuracy and Precision" and "A Generic Spectroscopic Instrument," two chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc I (double sided, 60 min.), Special Issue 3.

INSTRUMENTATION

1. Spectronic 20
2. Simple gas chromatograph
3. Microscopes; polarized light microscopes
4. Electrophoresis (gel)

Links/Connections

WITHIN CHEMISTRY

1. **Density**. A physical property. Because it is specific to the sample being measured (for example, glass), it can be used as a means of identification or comparison (see *Demonstration 1*).

Material	Density (g/mL)
Celluloid	1.4
Porcelain	2.3 - 2.5
Window glass	2.47 - 2.56
Headlight glass	2.47 - 2.63
Flint glass	2.9 - 5.9
Diamond	3.0 - 3.5

Figure 12. Density of common materials.

2. **Water of hydration**. A compound in which water is an integral part of the crystal structure of a salt contains water of hydration. Plaster of Paris (calcium sulfate, $CaSO_4 \cdot 1/2\ H_2O$) is used to make plaster casts. Prints from shoes and tires left in soil or sand can be preserved by making a plaster or plastic cast. When mixed with water, Plaster of Paris produces heat that drives off some of the excess water and leaves a solid product. When this mixture is poured into the depression left by a car tire or running shoes and allowed to harden, a cast can be obtained and compared to that of a suspected tire or running shoe.

$$2\ CaSO_4 \cdot 1/2\ H_2O(s) + 3\ H_2O(l) \rightarrow 2\ CaSO_4(s) + 4\ H_2O(l) + \text{Heat}$$

3. **Elemental analysis**
   a. Heavy metal poisons (lead, arsenic) are determined by atomic absorption spectroscopy (see Item 8).
   b. Bullet lead contains a variety of trace elements whose concentrations vary with the bullet's source. A fired gun leaves invisible traces of antimony and barium on the firing hand from the cartridge primer (the exploding substance that propels the bullet). Cotton swabs moistened with dilute nitric acid are used to collect gunshot residues. The swabs are analyzed using flameless atomic absorption spectroscopy. Recently, the scanning electron microscope has been used to search for particles with features consistent with the gunpowder particles (intact or partially burned) combined with elemental analysis for lead, barium, and antimony using X-ray fluorescence.
   c. A variety of trace elements in paint pigments creates a difference in paint samples. The identity and quality of an element (Pb, Ti, Cr) present in a paint chip can help identify the source. Elemental analysis is performed by X-ray fluorescence or atomic absorption spectroscopy (see Item 8).
   d. The main elements in glass are sodium, silicon, and oxygen. Other elements are added to give glass color or a special property. Sometimes the element is present because of the mineral from which the glass is made. These elements can be detected and quantified using X-ray fluorescence.

4. **Qualitative chemical tests**. Various routine chemical tests are used to identify gunshot residues, fabrics, drugs, blood, *etc.*

   a. Blood is usually detected by testing for heme (the porphyrin bonded to the protein portion of hemoglobin). Because heme acts as a catalyst, some tests for blood utilize hydrogen peroxide to oxidize compounds that result in a specific color change. For example, a stain can be identified as blood with a solution of phenolphthalein and hydrogen peroxide. This test depends on the fact that the hemoglobin present in the blood catalyzes the decomposition of hydrogen peroxide. The decomposition product oxidizes colorless, reduced phenolphthalein to pink-colored phenolphthalein.

   b. When concentrated nitric acid is placed on wool or silk, a yellow color (which can be intensified with ammonia) due to the formation of xanthoproteic acid is formed. Only protein fibers, *e.g.*, wool and silk, give a positive test.

   c. Smokeless powder contains nitrates. When a cartridge is fired and the powder burns, the nitrates are converted to nitrites. The presence of the latter on a fabric can help determine if a hole in the fabric was made by the passage of a bullet through the fabric. If the suspect weapon is available and the developed nitrite pattern is compared to patterns obtained from firing the weapon at known distances, the technique can be useful for determining a range of distance from the target to muzzle (homicide *vs.* suicide). To confirm nitrite, any particles remaining on the fabric surface are transferred to a chemically treated photographic paper that contains p-nitroaniline, 2-naphthol, and magnesium sulfate. Nitrite will form a red-colored complex with this mixture.

   d. Qualitative tests for typically encountered drugs are summarized in the following table.

Substance	Reagent	Positive Test
Opium alkaloids: heroin, morphine, codeine	Formaldehyde/sulfuric acid	Violet color
Cocaine	Cobalt thiocyanate	Blue, flaky precipitate
Amphetamine	Cobalt thiocyanate	Orange color
LSD	p -Dimethylaminobenzaldehyde	Blue color
Tetrahydrocannabinol	Vanillin/acetaldehyde/ethanol/ chloroform	Purple color in chloroform layer
Barbiturates	Cobalt acetate/isopropylamine	Red-violet color

Figure 13. Tests for common drugs.

5. **Solubility**. Many fibers can be identified by their solubility in selected solvents.

Fiber	Solvent
Acetate	Boiling glacial acetic acid
Silk	Boiling 45% sodium hydroxide
Nylon	50% Hydrochloric acid
Wool	Boiling 5% sodium hydroxide
Cotton	70% Sulfuric acid
Dacron	55-60% Dimethylformamide (room temp.)

Figure 14. Fiber solubility.

6. **Oxidation-reduction**. Most commercial items are marked by the manufacturer as a means of identifying them. Usually marking is done by stamping a serial number (or other code) on the item. Even if the marking is sanded off, the surface can be treated so that the marking reappears to some identifiable degree. In the case of objects made of iron, etching solutions are used to restore obliterated markings. Etching solution contains acid and copper(II) ions. Iron, under stress from the marking stamp, will dissolve rapidly compared to the remainder of the metal according to the chemical equation:

   $$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$

   This procedure requires patience, but the results are usually definitive for metal objects.

7. **Enzymes**. Can be used to identify body fluids. Acid phosphatase is an enzyme secreted by the prostate gland into seminal fluid. Because its concentration in seminal fluid is much greater than in other body fluids, its presence can be used to characterize human seminal stains. If this enzyme is present in a specimen obtained from a rape victim, it causes certain dyes to give red-brown to violet-colored complexes.

8. **Instrumentation**

   a. In X-ray fluorescence, the sample is subjected to an X-ray beam. The less energetic, fluorescent X-rays are emitted by the elements in the sample. The wavelengths of these X-rays are characteristic of the elements in the sample. The intensity of the X-ray at a particular wavelength is proportional to the concentration of the element in the sample. This technique leaves the sample intact.

   b. Bits of metal shavings or dust make good evidence. The metal is dissolved in acid and analyzed by atomic absorption spectroscopy. The intensity of light of a given wavelength that is absorbed by atoms of a given element that are heated in a flame is proportional to the amount of that element in the sample.

   c. Instrumental techniques are very useful for characterizing organic liquids—greases, oils, and gasoline. Gas chromatography (GC)-infrared spectrometry (IR) and GC-mass spectrometry (GC-MS) combinations are very useful for analyzing these organic materials.

      Gas chromatography separates the individual organic compounds in the sample. These compounds are graphically recorded as individual peaks as each compound emerges from a chromatographic column. The peaks can be identified by infrared spectroscopy or mass spectrometry.

      The infrared spectrometer gives a unique spectrum for each separated compound as the percentage of infrared radiation passing through a sample at different wavelengths.

      The mass spectrometer breaks up each separated compound into a unique mass spectrum. In mass spectroscopy the molecules are converted to charged ions by electron bombardment. Each ion has a unique mass to charge (m/e) ratio. The various ions are separated by their m/e ratio using a magnetic field and then detected. Results are shown graphically.

The figures shown are the infrared and mass spectra of cocaine. The advantage of the combination lies in the fact that both infrared spectra and mass spectra are stored in data banks. Infrared and mass spectra can be matched with reference spectra by computer, thus providing a positive identification of the various organic compounds in the sample.

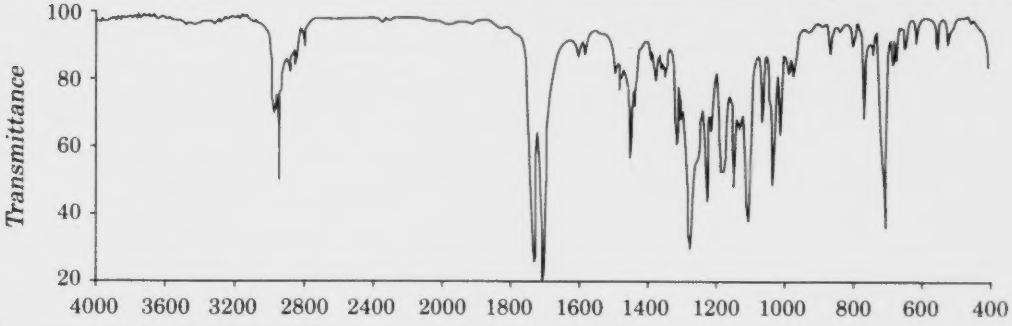
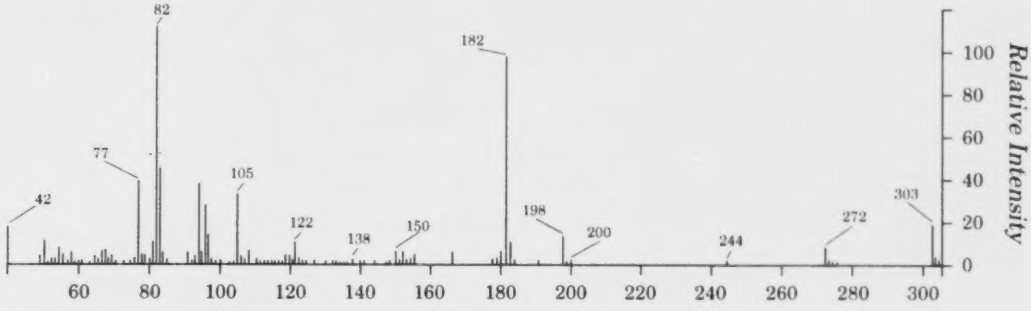


Figure 15. (a) Infrared and



(b) mass spectra of cocaine.

d. Highly flammable hydrocarbons are often used to start a fire as well as spread it. If the container (plastic, metal) that held the hydrocarbons is left at the arson scene, the debris and residues that are left after the container and contents have burned can be analyzed. The debris sample is placed in a container (a new, unlined paint can), sealed, heated to 60-110 °C to separate the hydrocarbon vapors from the debris. A sample of the air above the debris is removed by a syringe and analyzed by gas chromatography. This technique can often distinguish hydrocarbons in Diesel fuel, gasoline, charcoal lighter fluid, and paint thinner.

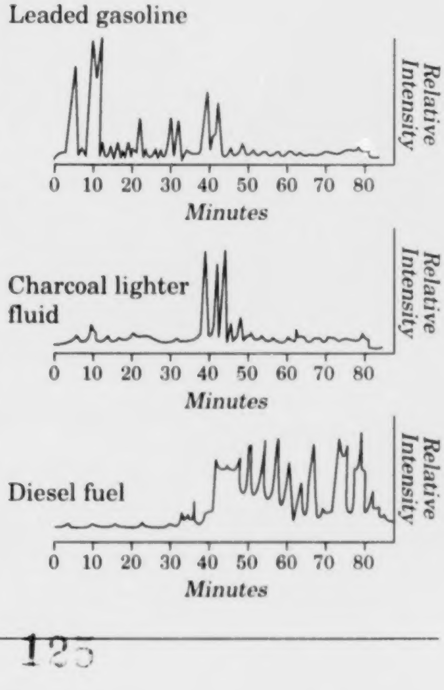


Figure 16. Gas chromatographic analysis of hydrocarbon mixtures.

e. In addition to colored chemical tests, analysis of drugs can be carried out by ultraviolet spectrometry, high-performance liquid chromatography and thin-layer chromatography.

In ultraviolet spectrometry, ultraviolet (UV) light of different wavelengths is passed through a sample, and the amount of absorbed light is recorded at each wavelength. The resulting absorption spectrum is characteristic of a particular drug (see Figure 17). The identity of the drug is generally confirmed using the specific chemical test.

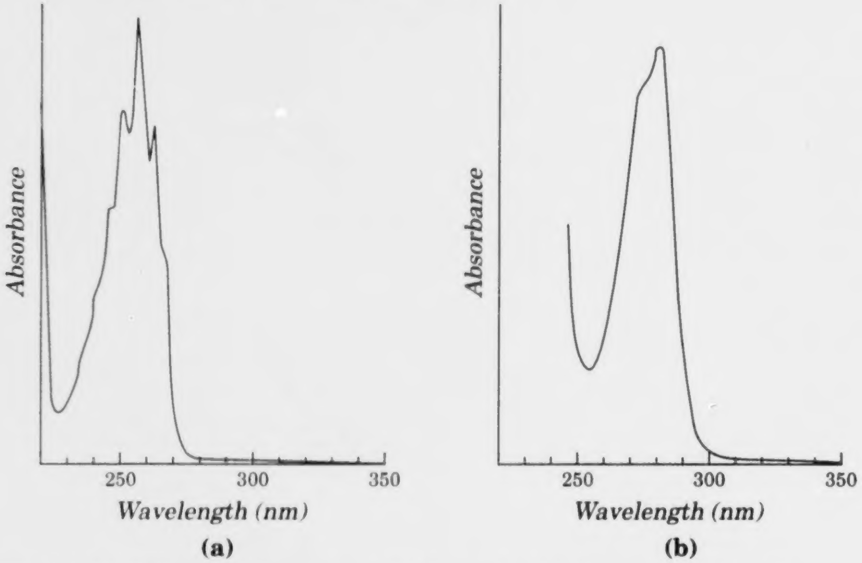


Figure 17. Ultraviolet spectra of (a) amphetamine and (b) heroin.

For drugs that do not vaporize without decomposition, high-performance liquid chromatography (HPLC) is used for identification. Instead of using gas to carry sample through the column (GC), solvent under high pressure is used.

Thin-layer chromatography (TLC) is a simpler analytical method. A separation is performed on a rectangular glass slide coated with a thin layer of adsorbent SiO_2. The sample is spotted at one end of the slide, and this end dipped into a solvent that rises up the slide as it soaks the layer of adsorbent. Different materials in the sample are carried at different rates and are separated. The spot can be made visible by treatment with iodine and/or ultraviolet light (black light). Some spots will fluoresce (*i.e.*, glow under UV light). The retention times of each spot are compared with those of known compounds and identified. In addition to drugs (see *Activity 1*), TLC can be used to identify lipsticks and ink dyes.

9. **Photography**. Useful in criminal investigation. Photography uses silver bromide (AgBr) suspended in a gelatin emulsion mounted on a plastic (cellulose acetate) support film. Exposing the silver bromide to light (when the camera shutter is opened), produces metallic silver and bromine (which then reacts with other materials in the film).

$$2AgBr + Light \rightarrow 2Ag(s) + Br_2$$

The dark silver particles produce an image that can be developed by further chemical processing. Color photography is a more complicated process.

10. **Explosives**. The criminal use of explosives is generally motivated by sabotage, mischief, revenge, or the desire to destroy property. Most bombing incidents involve the use of homemade explosives and incendiary devices. Forensic chemists are responsible for detecting and identifying both explosive chemicals and detonating mechanisms found at the crime scene. An explosion is a chemical reaction that proceeds at a rapid rate. There is a sudden buildup of large volumes of gas with enormously high pressures that cause a violent, physical disruption of the immediate environment. The decomposition of liquid nitroglycerin, produces four gaseous products, and is shown in the equation:

$$4CH_2(ONO_2)CH(ONO_2)CH_2(ONO_2)(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g)$$

Examples of explosives are shown in Figure 18. Nitrogen and oxygen are the key elements in these explosives.

Name of explosive	Chemical composition
Black powder	Potassium nitrate, charcoal, sulfur
Single-base smokeless powder	Nitrocellulose
Double-base smokeless powder	Nitrocellulose and nitroglycerin
Dynamite	Nitroglycerin and ethylene glycol dinitrate (for stability)
TNT	2,4,6-Trinitrotoluene

Figure 18. Composition of explosives.

There are several simple color tests performed to screen for the presence of explosives. The tests are usually done on acetone-water extracts. Common explosives (black powder is an exception) are organic compounds that tend to be soluble in this solvent mixture. One reagent, Griess reagent, consists of sulfanilic acid, acetic acid, and 2-naphthylethylenediamine.

Explosive	Griess reagent	Diphenylamine
Nitrate	Pink to red	Blue
Nitrocellulose	Pink	Blue-black
Nitroglycerin	Pink to red	Blue
TNT	No color	No color

Figure 19. Color tests for explosives.

If sufficient amounts of explosives are recovered, confirmatory tests may be performed by infrared spectroscopy or X-ray diffraction.

Explosives are also used for commercial purposes: to remove barriers for construction of a tunnel through a mountain, to help excavate earth for building foundations, to destroy old buildings to make way for a modern structure, and as propellants for rocket engines (controlled "explosions").

11. **Organic chemistry**. An organic compound, 1,8-diazafluorenone (DFO), has been found useful for detecting latent fingerprints. Now available to forensic science laboratories, DFO reacts with α-amino acids producing a red, fluorescent substance. DFO is 2-3 times more sensitive than ninhydrin and is very useful for detecting latent fingerprints on paper.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

1. **Physics**. In addition to color and density, refractive index is a useful way for identifying glass. Refractive index is the degree to which a beam of light bends as it passes from air into a solid or liquid.

Glass	Index of refraction
Pyrex™ glass	1.47
Headlight glass	1.47 - 1.49
Television glass	1.49 - 1.51
Window glass, bottles	1.51 - 1.52
Ophthalmic lenses	1.52 - 1.53
Light flint glass	1.6

Figure 20. Refractive indices for glasses.

2. **Geology**. Soil is a common form of physical evidence. Soil samples are analyzed to determine if they have a common origin. The methods include a density profile and settling rate curve. For example, a soil sample is dried and sieved. (Sieves containing 200 wires per in^2 = 200 mesh; 50 wires per in^2 = 50 mesh, *etc.* The higher the mesh size, the finer the particles.) A small amount of a desired mesh size (usually 30-45 g) is placed on the top of a column containing layers of immiscible liquids of different densities. Heavy particles will settle to their level in a few minutes. Light particles may take a few hours to stop moving. The soil profile at the scene is then compared to the soil profile from the suspect. (The same technique can be used to determine the density of small glass fragments.)

3. **Biological Science**. Blood contains characteristic factors based on blood groups. A person's blood contains proteins called antibodies. Human blood can be grouped into types A, B, O, and AB, depending upon the antibodies present in the serum. If blood from people of other blood types are mixed, agglutination (clumping together) will occur. All four types can be identified by this method. Blood typing can be useful (but not conclusive) in establishing possible parents of children.

   Blood proteins are controlled by genetics and are rather specific for an individual. The best tool for distinguishing blood proteins is electrophoresis. Proteins are electrically charged at a given pH. In the presence of an electric current and at the appropriate pH, the proteins migrate at different rates toward the positive electrode separating into different spots along the way. The spots are stained with ninhydrin, making them visible. Their relative positions are used to identify individual proteins (see *Enzymes* module).

4. **Biological Science**. DNA Profiling is a new technique that helps identify suspects from bodily traces (blood, semen, hair) often left at a crime scene. DNA consists of four bases attached to each other in pairs and connected like a zipper into a double helix pattern. The exact sequence of bases is unique to each person (except identical twins), somewhat like a fingerprint. To link a suspect to the crime, DNA is extracted from physical evidence found at the scene of a crime. Scientists split the DNA pairs into fragments and the fragments are separated into bands by electrophoresis. The fragments are mixed with radioactive bases that bind to the DNA as pairs as in the original sequence. When exposed to X-ray film, the DNA pattern appears in bands resembling a bar code on supermarket products. The DNA pattern from the evidence is compared to the DNA pattern in the suspect's blood sample.

TO THE CONTEMPORARY WORLD

1. **Court witness**. The forensic chemist is often called to testify as an expert in civil and criminal cases. In criminal cases, forensic chemists may be asked to explain the identification (chemical test, analytical instrumentation, reliability of test, *etc.*) of a drug found in the body of a deceased person. In civil cases, he/she may testify in cases involving water quality, product liability, *etc.*

2. **Driving while intoxicated (DWI) and the Breathalyzer**. The Breathalyzer has been shown to be a reliable, noninvasive instrument for forensic alcohol analysis. The chemistry of the Breathalyzer involves the reduction of orange potassium dichromate by ethanol contained in the breath of the test subject.

   $$3C_2H_5OH(g) + 2K_2Cr_2O_7(aq) + 8H_2SO_4(aq) \rightarrow$$
   $$3CH_3COOH(l) + 2Cr_2(SO_4)_3(s) + 2K_2SO_4(aq) + 11H_2O(l)$$

   The reduction product, $Cr_2(SO_4)_3$, is a green solid. The Breathalyzer scale provides a percent blood-alcohol concentration. A value of 0.10% is the minimum amount for being legally intoxicated and subject to a DWI conviction (see *Demonstration 1* in *Chemistry in Medicine* module).

3. **Computers**. In forensic laboratories computers can collect and store voluminous quantities of laboratory data. Minicomputers link local crime laboratories *via* telephone lines to large, perhaps national, computers. Such systems facilitate the collection of reference information on glass, paint, tire prints, shoe prints, and headlights. Computers can help with interpretation of data; instead of manually comparing and subjectively evaluating chromatograms of drugs, accelerants, paints, plastics, *etc.*, computers can be used to precisely scrutinize and compare samples to references by pattern recognition algorithms.

4. **Literature**. As forensic science developed in police laboratories, fiction writers began to base some characters in their novels on forensic scientists. Sherlock Holmes is perhaps the most popular fictional detective. He is noted for solving crimes by the application of science. He recognized the odor of iodoform, the black mark of silver nitrate on a finger, and readily confirmed Watson's diagnosis concerning the "pleasant almondy odor" of a "small blue bottle" as prussic acid in Arthur Conan Doyle's *The Veiled Lodger*. The chemical discovery of which Holmes is most proud is described in *A Study in Scarlet*. "'I've found it! I've found it!' he shouted, running toward us with a test-tube in his hand. 'I have found a reagent that is precipitated by hemoglobin and by nothing else.' In an instant, the contents assumed a dull mahogany color, and a brownish dust was precipitated to the bottom of the glass jar." [See Gillard, R. D. (1976). Sherlock Homes: Chemist. *Education in Chemistry,* p. 10.] However, Arthur Conan Doyle was surprisingly uninformed in science and Sherlock Holmes, as a scientific detective, perhaps was not really the scientist we thought. [See Asimov, I. (1983). *The roving mind, Part IV Science Opinion,* "Sherlock Holmes as a Chemist," Prometheus Books, Buffalo, NY.]

   Ian Rae [Dustcoats in dustjackets. (1983). *Chemistry in Britain, 19,* 565.] discusses other authors who use chemistry in their novels, including Austin Freeman whose *Famous Cases of Dr. Thorndyke* (Hodder and Stoughton, London, 1929; reprinted 1965) contains much chemistry. In this book, Freeman describes the Marsh test for arsenic, including its distinction from antimony (using hypochlorite), and a description of an attempted poisoning by atropine that relied on secretion of this substance in eggs of pigeons that had been fed belladonna.

Dorothy Sayers apparently had learned some chemistry and used it in several of her novels. *Strong Poison* (Gollancz Publisher, London, 1930) deals with the ability of a practiced arsenic eater to withstand a dose that kills his victim. There is also an account of the Marsh test for arsenic. In *The Documents in the Case,* Sayers and Robert Eustace base the apprehension of a murderer on the stereoisomers in poisonous mushrooms. The poisoning occurred with the racemic mixture, indicating the death was not accidental.

Forensic chemistry is mentioned in other poisoning whodunits. Thallium poisoning was discussed in Agatha Christie's *The Pale Horse* (Fontana, London, 1972; first published 1961). Ngaio Marsh's *Final Curtain* (Middlesex Penguin, 1961; first published 1947) gives a sketchy description of the chemistry of embalming and the flame test for thallium.

Many of J. J. Connington's stories involve forensic chemistry. Connington was the pen name of A. W. Stewart, a professor of chemistry at Queen's University (Belfast, 1919-1944). *The Counsellor* (Hodder and Stoughton, London, 1939) discusses mescaline trances and *Jack in the Box* (Hodder and Stoughton, London, 1944) contains a poisoning with nickel tetracarbonyl.

Forensic science techniques have been used in several recent fictional and nonfictional books. The following is a brief listing:

Ted Bundy: The Killer Next Door by Steven Winn
The Man Who Killed Boys by Clifford Linedecker
The French Connection by Robin Moore
Coma by Robin Cook
Fatal Vision by Joe McGinnis
The Third Deadly Sin by Lawrence Saunders
The Michigan Murders by Edward Keyes
The Boston Strangler by Gerald Frank
The Wood-Chipper Murder by Arthur Herzog

5. **Community Resources**

   a. Guest speaker from a local police department crime laboratory, the state crime laboratory, or the local medical examiner's office.

   b. Field trip to the local police department or crime laboratory.

   c. Guest speaker on uses of forensic chemistry in archaeology.

   d. Invite a race track tester or large-animal veterinarian for a classroom discussion on testing for drugs in horses.

   e. A museum curator is generally a good person to discuss art frauds.

Extensions

1. Examine the hairs of different people within a family, hairs of pets, *etc.*
2. Take broken glass samples from window pane, pop bottles, and headlight glass, and an unknown glass (from a roadway). Determine their densities using methods described in this module and try to identify the unknown glass.
3. Using a stereomicroscope, compare various paint chips (or flakes) obtained from cars in a junk yard. Mount the samples in putty or clay to hold on the scope and observe an edge to check for color layering.

References

Module drafted by Philip Ogata, James Schreck, and Courtney Willis, the Colorado (North) team.

Many ideas for laboratory activities in this module are from the personal collections of the following individuals. Their generosity in the use of their material is greatly appreciated and acknowledged.

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Barber, J. (1985). *Crime lab chemistry. Teacher's guide. Great explorations in math and science (GEMS).* Berkeley, CA: Lawrence Hall of Science, University of California.

An activity (chromatography, separating mixtures, pigments, and solubility) in which students assume the role of a crime lab chemist and determine which black pen was used to write a ransom note.

Benfey, O. T. (Ed.). (1969). *Chemistry, 42*(7). Washington, DC: American Chemical Society.

This entire issue is devoted to forensic science, including origins of modern criminology, scientific methods of crime investigation, and chromosomes and crime.

Robson, D. (Ed.). *ChemMatters.* Washington, DC: American Chemical Society.

Each issue contains a *Mystery Matters* feature that discusses an application of forensic science and chemistry to the real world.

Gerber, S. (Ed.). (1983). *Chemistry and crime: From Sherlock Holmes to today's courtroom.* Washington, DC: American Chemical Society.

Techniques used in crime novels both influence and reflect the scientific basis of crime detection.

James, R., Meloan, C., and Saferstein, R. (1980). *Laboratory manual for criminalistics.* Englewood Cliffs, NJ: Prentice Hall.

A set of laboratory experiments for the novice student that demonstrates what happens to physical evidence when sent to a forensic laboratory.

Labianca, D. (1990). The chemical basis of the breathalyzer: A critical analysis. *Journal of Chemical Education, 67,* 259-261.

Lewis, R. (1988). DNA fingerprints: Witness for the prosecution. *Discover, 9*(6), 44-52.

A new courtroom drama unfolds as the basic material of life itself is called to the stand.

* deceased, March 30, 1993

Manahan, S. (1982). *General applied chemistry* (2nd Ed.). Boston, MA: Willard Grant.

Chapter 21, "Chemistry and Crime," is an introduction to forensic chemistry.

Outlaw, H. E., and Berry, K. (Eds.). (1985). Forensic chemistry–A symposium collection. *Journal of Chemical Education, 62,* 1043-1060.

Pavia, D., Lampman, G., and Kritz, G. (1988). *Introduction to organic laboratory techniques* (3rd Ed.). New York, NY: Saunders.

Laboratory Activity 1 was adapted from this text.

Saferstein, R. (1990). *Criminalistics: An introduction to forensic science* (4th Ed.). Englewood Cliffs, NJ: Prentice Hall.

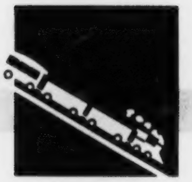
A presentation of the techniques, skills and limitations of the modern crime laboratory for the reader with no background in the forensic sciences.

Treat, L. (1981). *Crime and punishment*. Boston, MA: David R. Godine Publisher.

Twenty-four solve-them-yourself picture mysteries.

Zonderman, J. (1990). *Beyond the crime lab: The new science of investigation.* New York, NY: John Wiley & Sons.

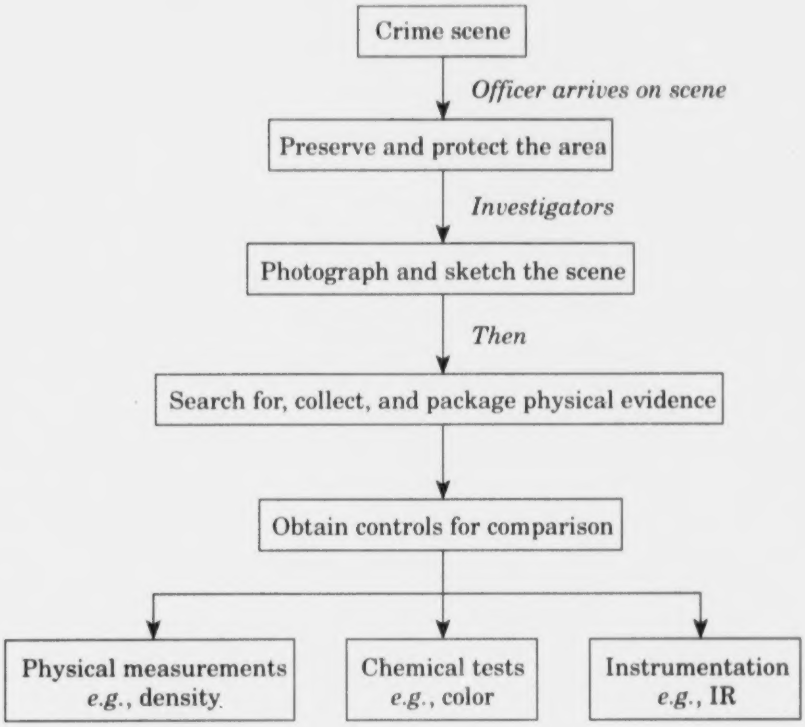
This book bridges the gap between the basic and advanced treatments of physical evidence in forensic sciences. It describes how computerized databases can help draw conclusions about victims and suspects, as well as how high-technology surveillance equipment can help keep a close watch on individuals under investigation.



Appendix

- **Transparency Masters**
  1. Flow Chart for a Criminal Investigation
  2. CLUE™ Logic Problem Data Table
  3. Word Search
- **Humor**

Flow Chart for a Criminal Investigation


Crime scene
Officer arrives on scene
Preserve and protect the area
Investigators
Photograph and sketch the scene
Then
Search for, collect, and package physical evidence
Obtain controls for comparison
Physical measurements e.g., density
Chemical tests e.g., color
Instrumentation e.g., IR

CLUE™ Logic Problem Data Table

MURDERER	WEAPON						ROOM									TIME						VICTIM					
	Pipe	Rope	Wrench	Candlestick	Knife	Revolver	Study	Hall	Lounge	Dining Room	Kitchen	Ballroom	Conservatory	Billiard Room	Library	12	2	4	6	8	10	Kelly	Lynn	Robin	Leslie	Dana	Chris
Col. Mustard																											
Miss Scarlet																											
Prof. Plum																											
Mrs. Peacock																											
Mrs. White																											
Mr. Green																											
Kelly																											
Lynn																											
Robin																											
Leslie																											
Dana																											
Chris																											
12																											
2																											
4																											
6																											
8																											
10																											
Study																											
Hall																											
Lounge																											
Dining Room																											
Kitchen																											
Ballroom																											
Conservatory																											
Billiard Room																											
Library																											

	SEX	
	M	F
Kelly		
Lynn		
Robin		
Leslie		
Dana		
Chris		

Word Search

```
B W Y Q P I K V E B C V T K J W T
Y P H G X X W P T A N A L Y S I S
P W W L O C J X M U U D G C H L K
O W G Z M L F E H J Q O S N E M M
C T L C C H O P I Y L P P I D C Y
S L M B S X A C S O P V G U N H D
O X U N C R T M I F M N L Q A M E
R X N J G M R B N X P C S I I R C
T B E Y C A Z L A U O S C K Z Z W
C X L P E X T T O T S T D K A U F
E O J R H C E I E L X A T Q M C U
P E I J L D S J G Y L J P Y A Y O
S F Z Y H P A R G O T A M O R H C
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Analysis technique used to separate mixtures into their component parts.
2. Another name for a lie detector.
3. Carrier of genetic information used by forensic chemists to match samples of body fluids to suspects (Abbrev.).
4. Separation technique using silica-coated glass or plastic plates (Abbrev.).
5. Technique used by forensic chemists to identify compounds by their interaction with radiation.
6. Forensic unit dealing with poisons or drugs.
7. Forensic unit dealing with blood, body fluids, hair, fibers, and botanical specimens.
8. Process of breaking down whole information available into its components.
9. Forensic unit that examines bullets, cartridge cases, and ammunition.
10. TV forensic chemist played by Jack Klugman.

"Take this handkerchief back to the lab, Stevens. I want some answers on which monster did this—Godzilla? Gargantua? Who?"

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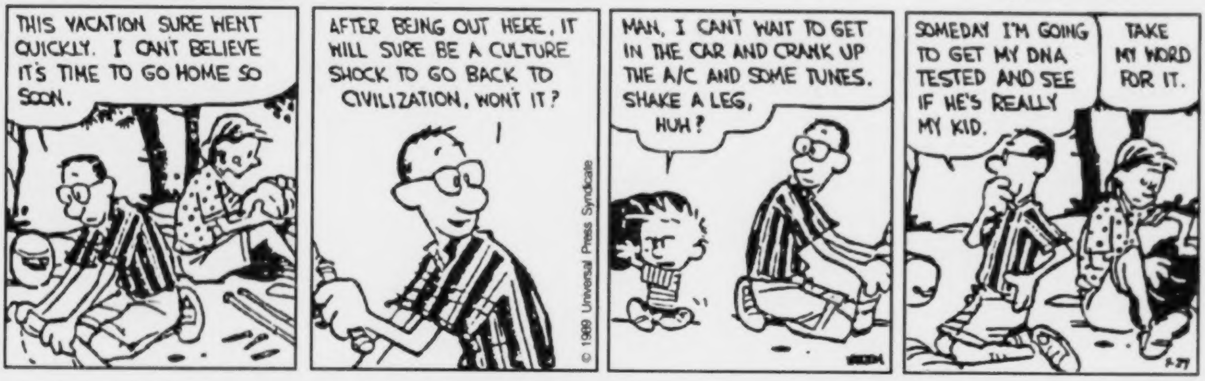
Calvin and Hobbes

by Bill Watterson


THIS VACATION SURE WENT QUICKLY. I CAN'T BELIEVE IT'S TIME TO GO HOME SO SOON.
AFTER BEING OUT HERE, IT WILL SURE BE A CULTURE SHOCK TO GO BACK TO CIVILIZATION, WON'T IT?
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MAN, I CAN'T WAIT TO GET IN THE CAR AND CRANK UP THE A/C AND SOME TUNES. SHAKE A LEG, HUH?
SOMEDAY I'M GOING TO GET MY DNA TESTED AND SEE IF HE'S REALLY MY KID.
TAKE MY WORD FOR IT.

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DOMOIC ACID POISONS CLAM EATERS

SO TROOPS... THEY FOUND OUT ABOUT OUR DOMOIC ACID TRICK! NEXT WE'LL MAKE DRANO!

CHEM 13 NEWS, May 1988, p. 18. Reprinted with permission.

A SourceBook Module

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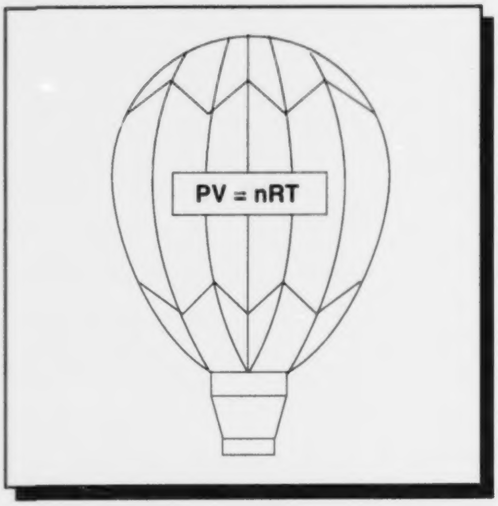
GASES



ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

Humans have been fascinated by gases since prehistoric times. Air was important enough to be considered one of the four elements by Aristotle—but only for about 200 years have scientists been able to distinguish one "air" from another and realize that the air we breathe is actually a mixture of gases.

Gases consist of submicroscopic particles that are relatively far apart from each other moving randomly with an average kinetic energy proportional to the temperature. (The word *gas* is derived from the Greek *chaos*.)

Gaseous particles have very little effect on each other; in fact an ideal gas particle is defined as having no volume and no attraction for other particles. We can show by our senses of smell or sight that gases spread out to fill a given volume.

Gases can be described in terms of four variables: pressure, volume, temperature, and amount (moles). Several sets of two variables—pressure and temperature (Gay Lussac's Law), volume and temperature (Charles' Law), volume and amount (Avogadro's Law), and pressure and amount—are directly proportional, but pressure and volume are inversely proportional (Boyle's Law). We can use simple logic to understand the relationships among these variables. Because gases are so much a part of our lives, many examples of these relationships are found in our environment.

The general gas law combines these variables into an equation with a single constant R, the gas law constant. The equation $PV = nRT$ may be used in calculations, assuming students have a background in algebra.

There are other relationships derivable from the gas law. Dalton's law of partial pressures indicates that the sum of the pressures of two or more gases equals the total pressure. For many years the molar masses of gases and volatile liquids were determined experimentally using the gas laws. Gas densities can also be calculated using these relationships.

From the time of the 18th-century revolution in chemistry, scientists have used the volumes of gases in work involving stoichiometry of reactions. That two volumes of hydrogen react with one volume of oxygen to form two volumes of water vapor helped chemists understand that H_2 and O_2 were diatomic and that H_2O was a better formula for water than was HO. This knowledge was essential to development of modern atomic theory.

PLACE IN THE CURRICULUM

Many secondary school texts use gases as an introduction to the atomic theory since gases, like atoms, are generally invisible bodies with observable effects. Using gas laws in stoichiometric calculations makes a link between different topics in the study of chemistry.

Whether it is concern with pressure in an automobile tire, the expansion of popcorn on heating, the effect of a leak in a space suit, the understanding of absolute zero, or the solution to environmental problems such as the depletion of the ozone layer, the study of gases enriches the curriculum of high school students.

CENTRAL CONCEPTS

1. A gas sample is composed of submicroscopic particles moving with an average kinetic energy directly proportional to the temperature (in kelvins).
2. A gas sample may be described in terms of four variables—pressure, temperature, volume, and amount (moles).
3. The general gas law describes relationships among the variables (P, T, V, n) of an ideal gas. Relationships often described in textbooks as Boyle's law, Gay Lussac's law, Charles' law, and Avogadro's law can be regarded as subsets of the general gas law.
4. The behavior of gases can be explained in terms of the kinetic molecular theory.
5. Gas densities and molar masses can be determined experimentally through applications of the general gas law.
6. Gas particles, when compared with those of liquids and solids, are relatively far apart from one another.

RELATED CONCEPTS

1. Mass, volume, pressure, temperature, amount of substance
2. Energy
3. Molecules and atoms
4. Stoichiometry
5. Variables, constants
6. Density
7. Molar mass

RELATED SKILLS

1. Problem solving
2. Algebra
3. Measurement
4. Graphing
5. Temperature scales

PERFORMANCE OBJECTIVES

After completing their study of gases, students should be able to:

1. imagine gases moving in a given volume at a given temperature and describe the behavior of an ideal gas.
2. define and/or explain the meaning of pressure, temperature, volume, and amount of substance (moles).
3. predict the result of changes involving two variables (P, V, n or T) when others are held constant.
4. use the general gas law in calculations, either in one- or two-condition problems.
5. use the general gas law to calculate molar mass and gas density.
6. understand the importance of gases in the environment.
7. recognize and discuss environmental problems concerning atmospheric gases or global warming.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Volume and Temperature Changes in a Gas

Introduction

Gases may be studied in relation to certain variables: pressure, volume, temperature, and amount (moles). In this laboratory activity we will develop a relationship between the volume and temperature of a gas sample and, by extrapolation, estimate the value of absolute zero, theoretically the lowest possible temperature obtainable.

Purpose

To determine the relationship between the volume and the temperature of a gas and to estimate the value of absolute zero.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Whenever a burner is used, care should be taken to avoid burns.
3. Do not leave thermometer in beaker between measurements.

Procedure

1. Completely fill an empty pipet with water.
2. Count the number of drops it takes to empty the pipet. (Repeat for better accuracy using a new pipet.)
3. Record the average number of drops. This number represents the volume of the pipet. It also represents the volume of gas at the higher temperature in this activity.
4. Fill a tray half full of water. Record room temperature. Adjust the temperature of the water until it equals that of the room.
5. Half fill the beaker with water. Heat until the water is about 20 °C above room temperature.
6. Holding a new pipet by the stem, immerse its bulb in the warm water in the beaker. Hold in the water for 1 min to allow the temperature of the air in the pipet become equal to that of the water.
7. Pinch the end of the pipet stem with pliers or a fingernail to seal it off. Record the temperature of the warm water in the beaker.
8. Fully submerge the pipet in the tray containing room-temperature water. Make sure that the stem is under the water and unseal. What happens in the stem of the pipet? Keep the pipet submerged until no further changes are noted (about 1 min).
9. Remove the pipet from the water and dry the outside. Count the number of drops of water that were drawn into the pipet. This number, subtracted from the original number, represents the volume of the air sample at the lower temperature.

10. Increase the temperature of the water bath by 10 °C and repeat the procedure using a *new, dry* pipet.
11. Repeat Steps 8-10 until a temperature of about 90 °C is reached.
12. Thoroughly wash your hands before leaving the laboratory

	Temp. °C	**Volume at higher Temp. (in drops) (Volume of empty pipet)**	**Volume at lower Temp. (in drops)**
Room Temp.			
1			
2			
3			
4			

Data Analysis

Prepare a graph of your data, with temperature (in degrees Celsius) on the horizontal axis (x axis) and total air volume in the bulb (in drops) at that temperature on the vertical axis (y axis). The x axis should be numbered from −350 °C to 150 °C. You will have two data points—involving a high- and low-temperature volume—to include on each line. Draw a straight line connecting each set of two points. Extend each line so that it intersects the horizontal axis (x axis). You will thus obtain several estimates of absolute zero—one for each graph line. Decide on a "best" estimate for absolute zero, based on your overall graph results.

Implications and Applications

1. What is the relationship between the volume and the Celsius temperature as shown on your graph?
2. Absolute zero theoretically measures the limit of molecular motion. What is the volume of an ideal gas sample at absolute zero?
3. If we created a new temperature scale where the value of absolute zero were zero, what would be the value of 0 °C?
4. Superconductors function best at very low temperatures, below the boiling point of liquid nitrogen (−195.8 °C). Select one of your graph lines. What would be the volume of that air sample at −195.8 °C?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Volume and Temperature Changes in a Gas

Major Chemical Concept

The volume of a gas sample is directly proportional to its absolute (Kelvin) temperature. The volume of an ideal gas theoretically becomes zero at –273 °C, or 0 K.

Level

This laboratory activity can be done by basic, general, and honors students.

Expected Student Background

Students should be aware of the variables (pressure, temperature, moles of substance, and volume) by which gas samples are described. They should know the relationship between gas temperature and its average kinetic energy. They should be reminded about construction of graphs and how to draw the best-fit line.

Time

If students work in pairs, the experimental work can be completed in 40 min. Additional time is needed for analysis of data.

Safety

No additional precautions.

Materials (For 24 students working in pairs)

12 Beakers, 800-mL, half filled with tap water (Allow to come to room temperature)
12 Trays or shallow plastic containers, containing enough water to cover pipet. (Allow to come to room temperature)
96 Plastic (Beral™) pipets, small, new. These must be dry. (Pipets may be obtained from many supply houses including Flinn Scientific Inc., Batavia, IL 60510.)
12 Thermometers (°C)
12 Burners
12 Ring stands with iron rings
12 Wire gauze
12 Pinch pliers

NOTE: A hot plate may be used in place of the burner and ring stand.

Advance Preparation

Remind students of the variables in the gas laws. In this activity, temperature and volume are measured, while pressure remains constant. Four graph lines are drawn; each data pair involves a sample with different gas amount (moles).

Pre-Laboratory Discussion

Before students start the laboratory activity, demonstrate how to fill the pipet and how to count drops. To fill, squeeze as much air as possible from the pipet and insert stem in water. There will be some trapped air; it can be removed by holding the pipet vertically (bulb down), squeezing out the air so the stem is filled with water, then inserting the stem in water to fill completely. The bulb must be squeezed very gently to count each separate drop. A typical pipet contains between 100 and 175 drops.

Suggested pre-laboratory discussion question: What happens to the volume of an inflated balloon when you place it in hot water or very cold water?

Teacher-Student Interaction

Students will need help filling their pipets. The best way to seal a pipet is to pinch it with a fingernail. Students should count drops carefully and be sure to use a new pipet for each determination. Students will need help drawing graphs—scaling should include temperatures in the range +90 °C to –300 °C.

Some suggested questions to pose to students during the activity: What gas are we using? *[Air—a mixture of nitrogen and oxygen gases with traces of other gaseous substances.]* What is being held constant in this laboratory activity? *[The pressure.]* How could we determine the pressure? *[Barometer]* Why do you need to keep the pipet stem below the water? *[To keep air from getting in or out.]* Why does some water enter the pipet as it cools to room temperature? *[When the air is heated the volume increases and some air leaves the pipet. As the pipet cools, the air contracts and draws some water into the stem.]* Do the four graph lines have the same slope? *[No]* Why do they all converge at approximately the same temperature at a "zero" volume? *[V is directly proportional to T (absolute temperature)—if V becomes zero, then T (absolute) also becomes zero, despite the amount of gas in the sample.]*

Anticipated Results

	Temp. °C	Volume at higher Temp. (in drops) (Volume of empty pipet)	Volume at lower Temp. (in drops)
Room Temp.	23	170	170
1	44	170	157
2	67	170	147
3	78	170	141
4	89	170	136

Graph of Sample Data

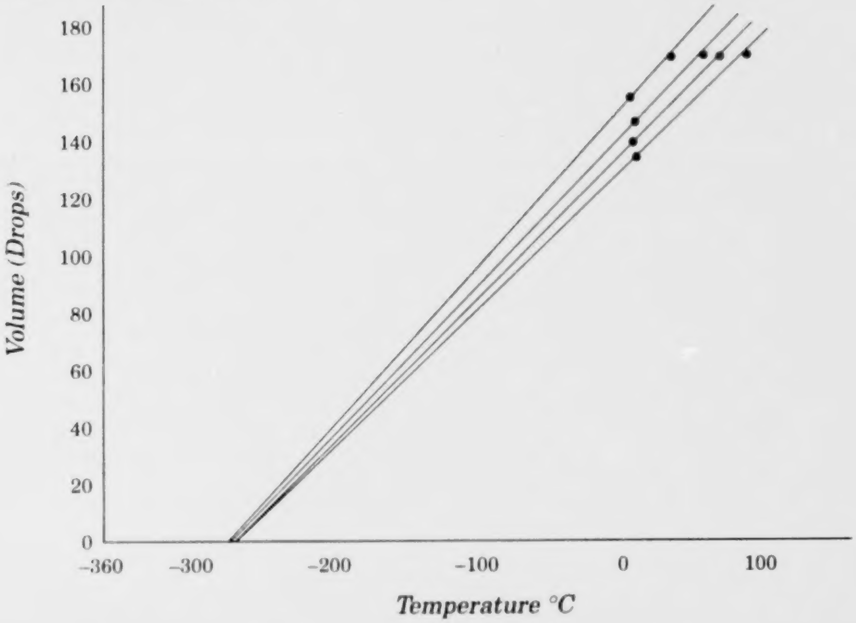


Figure 1. Temperature versus volume (drops) of sample data.

Answers to Implications and Applications

1. There is a direct relationship.
2. Volume is zero.
3. Guide students to draw new temperature scale along the side of graph starting at the intercept that should be about –300 °C. Give them the accepted value of –273 °C or 0 K. With the new scale, 0 °C would equal 273 K.
4. Can be found from students' graph.

Post-Laboratory Activities

1. Show sample problems that relate gas temperature to volume.
2. Use graph to determine temperature at which air will have a certain volume and *vice versa*.
3. Demonstrate Charles' Law using a 30-mL plastic hypodermic syringe. Trap about 20 mL of air inside and close with cap. Place syringe in hot water; measure the change in volume. Trap 10 mL of air and repeat, showing that graph of T-V slopes differ.
4. Have students convert temperatures from kelvins to degrees Celsius, and vice versa.
5. Discuss the concept of absolute zero and note that although molecular motion will cease, motion within molecules will continue.

Extensions

1. Have students complete a related activity using a syringe rather than a pipet. If two series are done, one with 10 mL trapped air and one with 20 mL, two lines will be obtained with different slopes. With more able students the slopes can be determined; they will differ by a factor of two due to the difference in the moles of gas:

   $PV = nRT$

   $V = (nR/P)T$ (nR/P) is a constant $= k$

   $V = (k)\,T$ $k =$ slope of plotted line on a V *vs.* T graph

   Thus, if n doubles, k (slope) doubles

2. Allow students to experiment with inflated balloons in a dry ice/isopropyl alcohol mixture (*CAUTION: extremely cold*) and in warm water, comparing balloon sizes.
3. Have students construct graphs from other data and determine the value of absolute zero. Use milliliters rather than drops for the volume units.
4. Charles discovered the temperature-volume relation for gases due to personal interest in balloons. Discuss the use of balloons in warfare and for domestic purposes before airplanes were invented.

Assessing Laboratory Learning

1. Use the questions suggested (in *Teacher-Student Interaction* section) on a test.
2. Have students determine the value of absolute zero from a graph constructed from other data.

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: Analyzing the 'Pop" in Popcorn

Introduction

Corn is a common foodstuff, native to the Americas, which appears in many forms: corn on the cob, corn off the cob, creamed corn, and popcorn. Field corn, which is also fed to livestock, is hung on our doors at Halloween. Each variety of corn contains different amounts of water, sugars, and starches. Popcorn is a favorite as an evening snack. Popping popcorn involves heating the corn until the pressure inside the kernel is great enough to cause it to burst, turning the kernel inside out and releasing the trapped moisture.

Purpose

To determine the percent water in popcorn, to use the ideal gas law to determine the pressure inside the kernel when it pops, and to solve gas law problems.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Heat the flask evenly to prevent spattering the oil.
3. Heat with care. Oil is flammable.
4. Do not eat the popcorn.

Procedure

1. Record the mass of a weighing cup.
2. Add 16 kernels of one type of popcorn and reweigh.
3. Calculate the mass of the popcorn kernels.
4. Using the water displacement method, find the volume of the 16 kernels using a 10-mL graduated cylinder. Dry the kernels.
5. Add two medicine droppers of cooking oil and the 16 kernels to an empty, dry 125-mL Erlenmeyer flask.
6. Determine the mass of the flask, oil, and popcorn.
7. Assemble a ringstand with ring, placing a wire gauze on top of the ring.
8. Using a utility clamp, fasten the flask to the stand so it sits on the wire gauze. Cover the flask with a piece of copper gauze. Bend the sides of the copper gauze around the flask's mouth.
9. Light the burner.
10. Hold the burner, moving it back and forth slowly until the popcorn just begins to pop. Remove the heat when most of the kernels have popped. *Do not burn the popcorn*. If you do, you'll need to start over.
11. If you see water condensed on the upper part of the flask, heat that part very gently with the burner until it disappears.
12. Let the flask cool, then remove and determine the mass of the flask and contents. (Remove the copper gauze before weighing.)
13. Thoroughly wash your hands before leaving the laboratory.

Brand Name ______________________

Mass of corn + weighing cup (g)
Mass of weighing cup (g)
Volume of water (mL)
Volume, water and corn (mL)
Mass of flask, oil, and unpopped popcorn (g)
Mass of flask, oil and popped popcorn

Sample Calculations Table

Mass of unpopped kernels (g)
Mass of popped kernels (g)
Volume of popcorn (mL)
Volume of popcorn (L)
Mass of water lost (g)
Moles of water lost
*Percent water in kernels
**Pressure of steam inside kernel at time of pop

Help with Your Calculations

Please show all work here:

$$\text{*Percent of water in "popcorn"} = \frac{\text{Mass of water lost}}{\text{Mass of 16 kernels}} \times 100$$

** To estimate the pressure of the water vapor at the time of "pop," use PV = nRT

Here are some hints regarding this calculation:

Step 1. Rearrange the equation to solve for P.

Step 2. Use the "moles of water lost" from the data table.

Step 3. R = 0.0821 L atm/(mol K)

Step 4. Assume that the popcorn pops at the boiling point of the cooking oil (225 °C) and convert this temperature to kelvins.

Step 5. Pressure will be in atm.

Implications and Applications

1. What brand of popcorn did you use?
2. What was the percent water in your popcorn?
3. Name one way in which popcorn, corn on the cob, and field corn are different.
4. What is the pressure of the water (as a gas) inside the popcorn just as it pops?
5. What was the atmospheric pressure in the laboratory during this activity?
6. Compare the pressure required to "pop" corn (Question 4) with atmospheric pressure (Question 5).
7. What assumptions have you made that might cause errors in your calculation of pressure?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: Investigating the 'Pop' in Popcorn

Major Chemical Concepts

This activity involves using the gas laws to determine the pressure inside popcorn kernels when they pop. Students will apply general gas law equations and discuss differences among various types of corn.

Level

This laboratory activity is written for a general or honors level student. It involves solving the gas law equation and requires algebra skills.

Expected Student Background

Prior to conducting this laboratory activity, students should have extensive practice with Boyle's law, Charles' law, combined gas law, ideal gas equation, the kelvin temperature scale, converting mass of water to moles of water, percent composition by mass, and using the water displacement method to determine the volume of irregular solids.

Time

A 55-min laboratory period is ample time to complete the activity. It will help to place needed hardware at laboratory stations and the oil and popcorn at a central location.

Safety

1. Vegetable oil is flammable. Students should heat the flask with care.
2. Students must fasten the ring onto the ring stand securely. The flask must also be securely fastened to the ringstand with a utility clamp.
3. Warn students not to eat the popcorn. Prepare other popcorn for them to enjoy outside the laboratory area.

Materials (For 24 students working in pairs)

12 Erlenmeyer flasks, 125-mL
12 Graduated cylinders, 10-mL
12 Copper gauze, or aluminum window screens, 1 piece, 5-cm x 5-cm
Pan balance
12 Ringstands
12 Iron rings
12 Wire gauze, 5" x 5"
12 Burners
12 Utility clamps
12 Packs of matches or flint lighter
12 Weighing cups, plastic

At a Central Location:

Cooking oil, 3-4 containers
3-4 Medicine droppers
Popcorn, 3-4 brands
Barometer (or call radio/television station for barometric pressure)

Pre-Laboratory Discussion

1. Provide samples of corn on the cob, corn off the cob, field corn, and popcorn for students to inspect. What are some differences among these types of corn?

2. Discuss the process of popping popcorn.
   a. When you heat popcorn, what happens to the water inside the popcorn kernels?
   b. Why don't some popcorn kernels pop?
3. What is the pressure of 0.010 mol of water vapor at 200 °C if it occupies a volume of 0.0020 L?
4. Calculate the pressure of the 0.010 mol of water vapor at 150 °C if its volume is held constant at 0.0020 L.
5. What is the relationship between pressure and temperature?

Teacher-Student Interaction

While circulating through the room, ask students questions such as: Do you expect the mass of popcorn to increase or decrease after it has popped? Why? *[The mass of the popcorn should decrease after it is popped because popping releases water vapor into the atmosphere.]* Do you expect the pressure inside popcorn kernels just before it pops to be greater than or less than atmospheric pressure? *[The pressure inside the kernels must be greater than atmospheric pressure to rupture the kernel "shell."]* What is the purpose of the cooking oil? *[The cooking oil surrounds and softens the kernel shell and provides a medium through which heat can be transferred from the glass to the popcorn.]*

Advance Preparation

1. Place all hardware at each laboratory station.
2. Place cooking oil, medicine droppers, and popcorn at a central location.
3. Decide whether all students should pop the same brand of popcorn or compare different brands of popcorn.
4. Prepare popcorn using a hot-air popper while students are completing the activity. Invite them to eat the popcorn *you* prepared, in a separate area, after they have cleaned all materials, washed their hands, and are working on the calculations.

Calculations

Mass of corn + weighing cup (g)	2.17 g
Mass of weighing cup (g)	0.17 g
Mass of popcorn (g)	2.00 g
Volume of popcorn (mL)	1.4 mL
Volume of popcorn (L)	0.0014 L
Mass of flask, oil, and "unpopped" popcorn (g)	80.7g
*Mass of flask, oil and "popped" popcorn (g)	80.5g
** Percent water in kernels	10%
*** Pressure of water inside kernel at time of pop (atm)	300 atm

*From this value (and the preceding value) students can find the mass of water lost in popping.

$$\text{**Percent water in kernel} = \frac{\text{Mass of water lost}}{\text{Mass of 16 kernels}} \times 100 = \frac{0.2\text{ g}}{2.0\text{ g}} \times 100 = \mathbf{10\%}$$

***Pressure inside kernel at time of pop. Use $PV = nRT$; solve for P.

$$n = 0.2\text{ g} \times \frac{1\text{ mol H}_2\text{O}}{18\text{ g}} = 0.01\text{ mol H}_2\text{O}$$

$$P = \frac{nRT}{V} = \frac{(0.01\text{ mol})(0.0821\text{ L}\cdot\text{atm}\cdot\text{mol-1}\cdot\text{K-1})(273 + 225\text{ K})}{0.0014\text{ L}}$$

$$P = 292\text{ atm, or } 3 \times 10^2\text{atm}$$

Answers to Questions

Pre-Laboratory Discussion Questions

1. a. Different types of corn contain varying amounts of water. Corn on the cob and corn fresh off the cob contain the largest percent water. Popcorn and field corn contain less water. Fresh corn on cob will not work as popcorn because there is no hard kernel to allow pressure buildup.
2. a. When the popcorn is heated, water in the kernels becomes hotter and vaporizes.
   b. Unpopped kernels possibly were too dry (insufficient moisture) and failed to build up sufficient pressure to pop, or had porous shells allowing gas to escape.
3.

$$P = \frac{nRT}{V} = \frac{(0.010\text{ mol})(0.0821\text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273 + 200\text{ K})}{0.0020\text{L}}$$

$$P = 1.9 \times 10^2\text{ atm}$$

4.

$$\text{Use } \frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \frac{(1.9 \times 10^2\text{ atm})}{(273 + 200\text{ K})} = \frac{x}{(273 + 150\text{ K})}$$

$$x = P_2 = 1.7 \times 10^2\text{ atm}$$

Answers to Implications and Applications

1. Answers will vary depending on the brand used.
2. Answers will range from 2% to 10% water.
3. Corn on the cob contains a much larger percentage of water. Field corn and popcorn contain much less water.
4. The pressure inside the popcorn will vary greatly. Answers should, however, range from 100 to 350 atm.
5. Read barometer and convert to atmospheres.
6. It is much larger.
7. Throughout the laboratory activity, the volume of popcorn kernels was assumed equal to the volume of displaced water. The pulp of the popcorn occupies much of the space inside the kernel; the volume recorded is larger than the actual volume occupied by the water. The kernel temperature at the time of popping was not directly measured. The assumption of 225 °C used in calculations is probably not highly accurate. Thus, for all these reasons, calculated results contain some degree of error.

Post-Laboratory Activities

1. Compile a class data table for all calculated pressure values at time of popping. Find the class average.
2. If different popcorn brands were used, compile separate class data tables. Then compare average pressures for each brand.

Extension

1. Students might enjoy investigating the production of popcorn and find the percent moisture in various types of corn. *[Popcorn is harvested at 16-19% water and dried to 13-14% water.]*
2. Discuss reasons for safety concerns if aerosol cans are brought too near heat or flames.
3. Discuss why your ears "pop" when riding in a plane that changes altitude.
4. Why is it sometimes suggested (in cold climates) to let out a small amount of air from automobile tires in the summer and to add air in the winter?
5. Discuss the operation of a tire gauge.

Assessing Laboratory Learning

1. How does heating popcorn affect the pressure inside the popcorn? *[As the popcorn heats, the water in the kernel vaporizes with about a thousandfold increase in volume. (The volume of 1 mole of liquid water is 18 mL whereas a mole of vapor is about 22000 mL). Since it is confined, the volume can't increase but pressure will, in direct proportion.]*
2. a. Name four variables that characterize a confined sample of gas. *[Pressure, volume, temperature and number of moles are the variables that describe any sample of gas.]*

   b. Which variables can be solved for by using the ideal gas equation? *[The ideal gas equation includes all of these: $PV = nRT$.]*
3. What mass of oxygen gas (in grams) is in a 2-L container of this gas at 25 °C and pressure of 2 atm?

   $V = 2\ L$
   $T = 298\ K$
   $P = 2\ atm$
   $mass = ?$
   $substance = O_2;\ MM = 32\ g/mole$

   Since mass is dependent on moles, find n.

   $$n = \frac{PV}{RT} = \frac{(2atm)(2L)}{0.0821\ L\ atm/mol\ K\ (298\ K)}$$

   $n = 0.16\ mole$
   $mass = (MM)(n) = (32\ g/mole) \times 0.16\ mol = 5.1g$
4. The contents in a 20-L propane tank at 25 °C exerts a pressure of 4.0 atm. What would the pressure in the tank become if the temperature were raised to 50 °C?

   $V = 20.0\ L$
   $T = 298\ K$
   $P = 4.0\ atm$

Since tank volume and moles are fixed and $PV = nRT$, *then* $\frac{P}{T} = \frac{nR}{V}$ = *constant; thus*

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P2 = P_1 T_2 / T_1$$

$$= 4.0\ atm \left(\frac{323\ K}{298\ K}\right)$$

NOTE: Most climatic temperature changes result in minor pressure changes.

DEMONSTRATIONS

Demonstrations on Gases, Balloons, and Bags

1. Blow up balloons with different gases.
   a. Contrast diffusion of gas through pores of rubber balloons and Mylar balloons. *[The Mylar balloon will stay inflated longer.]*
   b. Use sublimed dry ice (CO_2), methane (from natural gas jet) and air in different balloons. Note rate of fall to show difference in gas densities. (Can also be done with plastic bag.)
2. Put drops of vanilla extract in balloon prior to inflation to illustrate that the balloon is porous. You can smell the vanilla outside the balloon.
3. a. To illustrate atmospheric pressure, place a small amount of water (~100 mL) in an opened, emptied aluminum soda pop can. Heat the can until the water is boiling vigorously. Using beaker tongs, lift the can off the ring stand and quickly invert the can in a large tray of cold water. It will implode with "considerable vigor." (Plan to have several empty cans on hand; students will request an encore performance.) Calculate the moles of steam present at 100° C. Assume same number of moles of liquid water. Have students compare the volume of steam in the can with the volume of liquid water it forms.
   b. Put a one-gallon plastic bag into a one-quart wide-mouth container (mayonnaise or peanut butter jar) with the plastic bag lapping over the bottle neck. Smooth the plastic bag out against the inside surface of the jar, then fasten the bag tightly around the neck with a rubber band. (See the following illustration.) Ask students to pull the plastic bag out; they will be unable to do so!

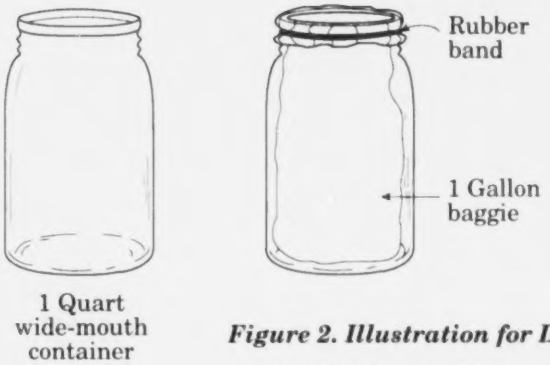


Figure 2. Illustration for Demonstration 3b.

4. Weigh 44 g of dry ice; place in empty garbage sack. Close the bag and watch it expand. (This illustrates the molar volume of a gas—in this case one mole of carbon dioxide.) 22.4 L is about 24 quarts or 6 gallons.
5. A water-filled balloon (or plastic bag) is drawn into a warm bottle as gas in bottle cools. A hard-boiled egg may also be used. (*NOTE: Warm the bottle with hot water. Cool in ice water.*) Place water-filled closed balloon or bag over opening of bottle and allow air in bottle to cool. As it cools, the pressure decreases and atmospheric pressure pushes the object into the bottle.

Bell Jar Demonstrations

1. Using a vacuum pump, evacuate a bell jar containing a small quantity of shaving cream or a marshmallow. Expansion rules!
2. Obtain a small vial (without cap). Put a bit of shaving cream in vial mouth to "plug" the opening. Place vial in the bell jar. Evacuate the bell jar and watch the shaving cream expand.

GROUP AND DISCUSSION ACTIVITIES

Diffusion and Convection

1. Pictures in the mind of gas filling a room.

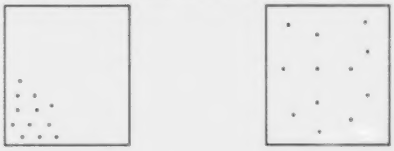


Figure 3. Gas filling a room.

2. Pictures and discussion of formation of ammonium chloride, NH_4Cl:

$$\underset{\text{Gas}}{HCl(g)} + \underset{\text{Gas}}{NH_3(g)} \rightarrow \underset{\text{White solid}}{NH_4Cl(s)}$$

The solid is formed closer to the HCl source because the less dense gas (NH_3) diffuses faster.

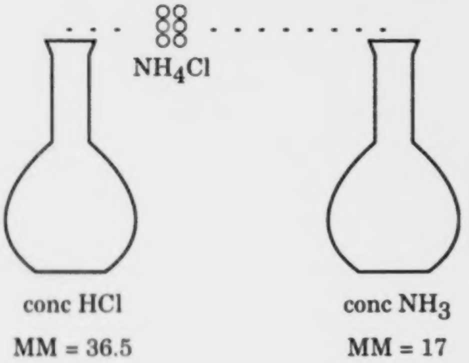


Figure 4. Formation of NH_4Cl from HCl and NH_3.

Pressure = Force/Area

1. **Difference between spike heel and large heel**. Because spike heel has smaller area, it will exert more pressure on the floor than large heel, assuming the force (body weight) is the same.
2. **Atmospheric pressure** (effect on body, changes on mountain). Compare to changes of state. Atmospheric pressure decreases as you move away from the earth because there are fewer gas molecules per unit volume. At high altitudes, we may have trouble breathing because of a lower O_2 concentration and because of the reduced pressure. The reduced pressure also affects the change from liquid to gas; the boiling point is lowered because the atmospheric pressure is lower. (Boiling point is the temperature at which the vapor pressure equals atmospheric pressure). Cake mixes will have different directions for higher altitudes. (Show cake mix box.) It also takes longer for boiled foods to cook at high altitudes due to the lowered boiling point.
3. **Design and use of a barometer** (construction of barometer involves safety hazards). Convert barometric pressure in inches of mercury to cm Hg, to mmHg.

   1 inch = 2.54 cm.
4. **Measure blood pressure**
5. **Question**. How tall would a barometer column under one atmosphere pressure need to be if the column were filled with water, not mercury? *[13.53 x 760 mmHg = the ratio of density of Hg to that of water]*

Temperature

1. **Discussion of Kelvin scale in relation to pressure and volume**. Temperature on Neptune –450 °F. Calculate in kelvins. Does this prove or disprove the concept of absolute zero?
2. **Relate temperature to kinetic energy**. Temperature is related to the average kinetic energy (motion) of molecules. Kelvin temperature is proportional to the kinetic energy.
3. Discuss difference between heat and temperature. Draw pictures of filled tea cup and filled bathtub. If at the same temperature, which contains more heat?

Pressure *vs.* Temperature.

1. Auto tires in summer and winter. You may need to let air out to decrease pressure in hot weather. Add air in cold weather.
2. Why does a bicycle pump get hot when you use it?

Volume *vs.* Temperature.

1. Hot-air balloons. What happens if the hot-air balloon heater malfunctions? If the air cools, its density will increase and the balloon gas will no longer be "lighter" (less dense) than air.
2. When gases are produced suddenly with the accompanying release of energy, explosions occur. This is how gun powder propels bullets, and it explains the force produced by rocket fuel. A typical rocket reaction:

$$\underset{\text{Hydrazine}}{2N_2H_4(l)} + \underset{\substack{\text{Nitrogen}\\\text{tetroxide}}}{N_2O_4(g)} \rightarrow 4H_2O(g) + 3N_2(g)$$

Notice the relatively large number of moles of gas produced.

Pressure *vs.* Volume.

Syringe: As you push in plunger of a sealed syringe (increasing pressure), the volume decreases.

Amount of Gas *vs.* Volume.

1. Blow up auto or bicycle tire, blow up balloon. This adds more moles of gas (n increases); the volume increases.
2. Avogadro's Law. Avogadro's law states that equal volumes of gases at the same temperature and pressure contain the same amount of gas. One mole of any gas at standard temperature and pressure (1 atm and 0 °C) occupies 22.4 L. Use general gas law ($PV = nRT$) to calculate this value.

Amount (Moles) vs. Pressure.

1. Pressure is used by anesthesiologists to measure amount of gases. When you buy gases such as helium in cylinders of fixed volume, the amount of gas can be calculated from the pressure (assuming temperature and tank volume are known). Gases are very difficult to weigh; pressure is easy to measure, so it is simpler to use pressure to determine the amount of gas.
2. When you add air to an auto tire, you increase the gas pressure in the tire.

Gas Densities

Balloons, dirigibles, and blimps float in air because they contain gases that are less dense (lighter) than ordinary air. Helium, hydrogen, or hot air may be used. The densities of these gases are all less than the surrounding air, since the mass of gas in a given volume is less. When unconfined air is heated, its molecules move faster (on average) and the volume expands. Hydrogen and helium have lower molar masses than most gases composing air (such as oxygen, nitrogen, water vapor, carbon dioxide, *etc.*). Dirigibles were used often in World Wars I and II for observation and transportation. Germany used hydrogen gas because it had no access to helium, which is found in large quantities in the U.S. Hydrogen is very explosive; the German airship *Hindenberg* exploded near Lakehurst, New Jersey in 1937, with great loss of life.

Mixtures of Gases and the Atmosphere

The atmosphere is a mixture of 80% nitrogen and 20% oxygen with traces of argon and other gases. Total atmospheric pressure is the sum of pressures of each individual gas. Even though oxygen and nitrogen have different densities, they mix completely in the atmosphere because of the ability of a gas to fill any space it occupies.

Analogies and Metaphors

1. Use plastic ruler. Hang sign indicating temperature (*T*) in middle. Show that if *T* is constant, see-saw effect takes place and *P* is inversely proportional to *V*. If *V* is held constant, increasing *P*, increases *T*, *etc.*

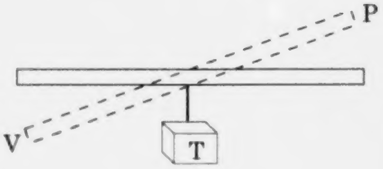


Figure 5. Seesaw analogy.

2. The analogy of a school dance can be used to illustrate many gas relationships. If you increase the size of the room (volume), the pressure of dancers decreases.

Pictures in the Mind

The study of gases provides a good example of relationships among variables and the identification of variables and constants. It also provides excellent opportunities to create "pictures in the mind."

General Questions

1. Predict what will happen as you change certain conditions of gases, holding other conditions constant (see *Tips for the Teacher*).
2. How can you determine the molar mass of a gaseous substance? *[If you measure the mass of a sample of gaseous substance at a known temperature, pressure, and volume, it is possible to determine the molar mass using the general gas law,* PV = nRT. *Using the known temperature, pressure, and volume, the amount (moles) of gas can be calculated. The measured mass divided by the amount of gas provides the molar mass. See* Tips for the Teacher *for further explanation.]*
3. What is an ideal gas? *[One in which the molecules occupy no volume and in which there are no attractions among molecules. Of course this is an ideal, not a real, situation, but real gases at room temperature and standard atmospheric pressure (1 atm) can behave nearly ideally since their molecules are so far apart. When gases are under high pressure and low temperature, their molecules come closer together and no longer act ideally.]*
4. Why is it necessary to change the temperature scale to kelvins in applications of gas laws? *[So that "zero" on the temperature scale represents the lowest possible temperature. With such a temperature scale, ideal gas volume is directly proportional to temperature.]*

TIPS FOR THE TEACHER

Language of Chemistry

absolute zero temperature at which molecular motion ceases; 0 K = 273.15 °C.

barometer device used to measure atmospheric pressure.

Boyle's law states that the volume of a fixed amount of gas at a constant temperature is inversely proportional to its pressure.

Charles' law states that the volume of a fixed amount of gas at a constant pressure is directly proportional to its absolute (kelvin) temperature.

gas form or state of matter in which a material assumes the shape of its container and expands to fill the container (thus having neither definite shape nor volume).

gas constant (R) numerical constant appearing in ideal gas equation ($PV = nRT$).

ideal gas one whose behavior can be predicted by the ideal gas equation.

ideal gas equation relates the pressure, volume, temperature, and amount of gas through the expression $PV = nRT$.

manometer device used to measure the pressure of a gas, usually by comparing the gas pressure to barometric pressure.

non-ideal gas departs from the behavior predicted by the ideal gas equation. Its behavior can only be predicted by other equations of state.

partial pressure pressure exerted by an individual gas in a mixture, independently of other gases.

Common Student Misconceptions

Misconceptions such as those listed are best dispelled with demonstrations followed by class discussion.

1. **"There cannot be any pressure around us, since we cannot feel it."**
   a. In an airplane you can feel the pressure in your ears, particularly during take offs and landings. When opening a soda can you can hear the change in pressure as the gas escapes.
   b. Demonstrate the breaking of a ruler covered with one sheet of newspaper by placing a cheap yardstick on a table with about half of it extending past the edge. Carefully spread a full page of newspaper over the portion of the yardstick on the table. (Press paper against the yardstick to expel air, smoothing the paper flat against the tabletop.) Then, with a karate-like blow, chop off the portion of the yardstick that extends beyond the table. Students can calculate amount of pressure on newspaper.

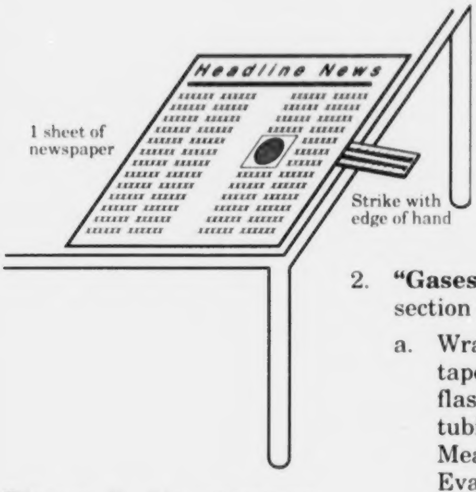


Figure 6. Air pressure demonstration set up.

2. **"Gases do not weigh anything."** (See *Demonstrations* section of module.)
   a. Wrap a 250-mL Erlenmeyer flask with strips of masking tape to prevent injury in case of an implosion. Fit the flask with a one-hole stopper, a 5-cm piece of glass tubing, and a 5-cm piece of rubber tubing with a clamp. Measure the mass of the assembly when full of air. Evacuate moderately with a vacuum or hand pump. Fasten clamp tightly and quickly weigh again to show the loss of mass. Demonstrate that the assembly returns to its original mass when the clamp is opened.

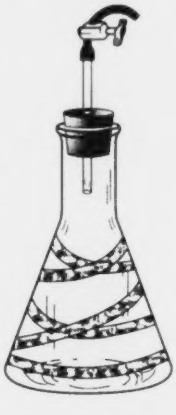


Figure 7. Wrapped Erlenmeyer flask.

b. Set up a balloon balance and add air to one balloon and CO_2 or methane to the other. The balance will tip to the side containing the higher-density gas sample.

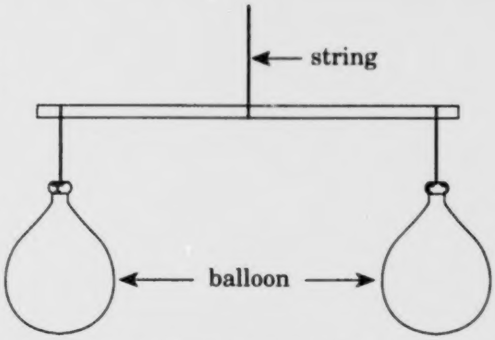


Figure 8. Balloon balance set up.

3. **"Hand me an empty glass."**

This demonstration shows that the air will be displaced by water flowing into the flask; thus, the flask was not really "empty". This demonstrates also how gases can be collected "over water," provided the gas is not very soluble in water. (Hydrogen and oxygen can be collected this way; chlorine, ammonia and hydrogen chloride cannot.)

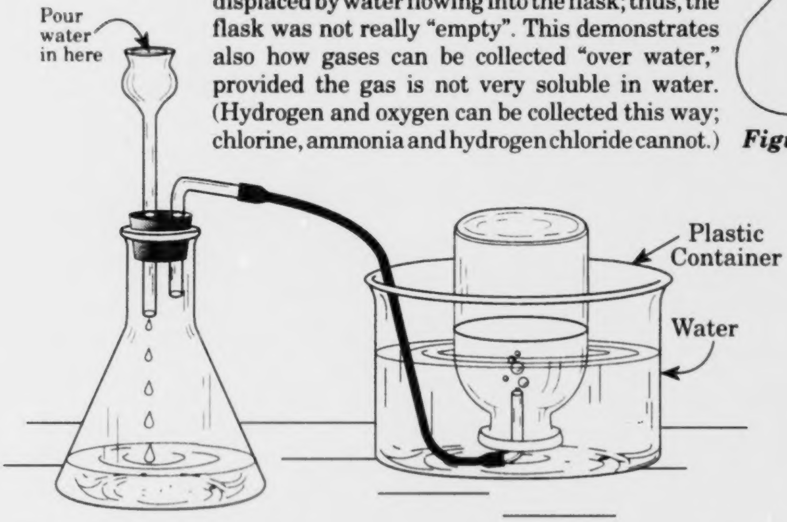


Figure 9. Apparatus to demonstrate water displacement by air.

4. **"When a gas expands the particles get larger."**

The molecules of a gas sample stay the same size, but distances between the molecules get larger when the sample expands.

Problem Solving

Although many texts approach the gas laws as separate conditions, with separate equations such as $P_1V_1 = P_2V_2$ for students to memorize and use; these concepts can also be taught in terms of only one equation, $PV = nRT$.

Because some students may not have an adequate background in algebra, presenting the gas laws logically will help them understand these concepts. For instance, if the two variables are pressure and volume (the text may call this Boyle's law) we know that they vary inversely. As one increases, the other decreases. Therefore we can determine logically the direction of the change. It is useful to start by setting up a data table:

Example: What will the final pressure of a gas sample be if it is initially at 2.0 atm and the volume is changed from 42 L to 124 L at constant temperature?

Remember that T must always be in kelvins (or other absolute temperature scale). Students should predict whether the pressure will increase or decrease (if volume increases, pressure will decrease) and set up the relationship accordingly.

2.0 atm (42 L / 124 L) = ? atm

The fraction must be less than one to realize a decrease in pressure.

	Condition I *(initial)*	**Condition II** *(final)*
P	2.0 atm	? atm
V	42 L	124 L
n	Constant	Constant
T	Constant	Constant

If the two variables are pressure and temperature (Gay-Lussac's law), they are directly proportional. As one increases the other increases.

If the two variables are volume and temperature (Charles' law), they are also directly proportional.

If there are more than two or more variables, each set or pair should be treated individually, either in two steps (using two tables) or in a combined equation.

Example: What is the volume of a gas sample at 0.95 atm and 25 °C, if its volume is 26 L at 1.2 atm and 14 °C?

First, use the relationship between *P* and *V*. Since the pressure *decreases*, the volume will *increase*.

	Condition I *(initial)*	**Condition II** *(final)*
P	1.2 atm	0.95 atm
V	26 L	? L
T	14 °C + 273 = 287 K	25 °C + 273 = 298 K
n	Constant	Constant

26 L (1.2 atm/0.95 atm) = 33 L

If the temperature *increases*, the volume will also *increase*. Use the new volume found above:

33 L (298 K/287 K) = 34 L

If the table shows that only one set of conditions is involved, then *PV=nRT* should be directly used.

Example: How many moles of a gas will occupy 2.7 L at 36 °C and a pressure of 0.95 atm?

	Condition I *(initial)*	**Condition II** *(final)*
P	0.95 atm	-
V	2.7 L	-
n	?	-
T	36 °C + 273 = 309 K	-

Note that all units used must match those in the constant (R).

$$PV = nRT \qquad n = PV/RT$$

$$n = \frac{(0.95\ \text{atm})\,(2.7\ \text{L})}{(0.0821\ \text{L}\cdot\text{atm}\cdot\text{mol-1}\cdot\text{K-1})\,(309\ \text{K})} = 0.10\ \text{mol}$$

Note that all units used must match those in the constant (*R*).

	Condition I *(original problem)*	**Condition II** *(STP)*
P	0.95 atm	1 atm
V	2.7 L	22.4 L
n	? mol	1 mol
T	36 °C + 273 = 309 K	273 K

If students lack the algebra background to complete such one-condition problems, suggest that they set up such problems using the molar volume of gas at standard temperature and pressure. This will allow them to treat it the same way as previous problems.

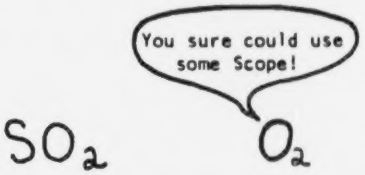
HISTORY: ON THE HUMAN SIDE

1. Robert Boyle (1627-1691) was the son of one of the richest men in England, who had made his fortune acquiring land in Ireland, some of it from Sir Walter Raleigh. The wealth of his father allowed Boyle the leisure to become a scientist; his talent at experimentation resulted in many new insights into nature. He was a chemist as well as a physicist and approached the study of science in a manner more modern than most of his contemporaries.

2. Before development of airplanes, balloons were a common type of airship. The French were pioneers in ballooning, beginning with the historic ascent by the Montgolfier brothers in 1783 in a hot air balloon. In the same year Charles introduced hydrogen gas that caused the balloon to rise without a burner. During the wars of the French Revolution, balloons were used as observation posts, although they were difficult to steer and were not used as transport. Gay-Lussac's ascents in 1804 were the first scientific expeditions using balloons. Readings of temperature, pressure, humidity, and of magnetic field were taken as well as samples of air, which were later analyzed. Gay-Lussac's ascent broke a record for altitude—7 km above sea level—which was not surpassed for nearly 50 years.
3. Boyle discovered the relationship between the pressure and the volume of a gas in 1662, but Charles and Gay-Lussac did not state the relationship between temperature and volume or temperature and pressure until about 1800. Why? Because accurate thermometers were not available.
4. Individual gases were not discovered until late in the 18th century. Oxygen was first recognized by C.W. Scheele in Sweden, but his work was not published until after that of Joseph Priestley, an Englishman, who was forced to leave his native country in 1794 because of his political beliefs. Priestley also described carbon monoxide, sulfur dioxide, and ammonia. Henry Cavendish, the eccentric grandson of a Duke, isolated hydrogen and nitrogen.
5. About 50 years ago, the scourge of polio appeared each summer, with an annual average of 21,000 cases of crippled Americans. An effective vaccine was developed in 1955 and polio virtually disappeared. Iron lungs were invented to help victims who had their diaphragms paralyzed by the disease. Many polio victims lived for years in these artificial respiration machines, which used pressure to draw air in and out of the lungs.

HUMOR: ON THE FUN SIDE

1. Student responses on an exam:
   a. Hydrogen is often found in snow and rain water.
   b. Hydrogen is prepared by freezing air.
   c. Hydrogen is produced by formation of sugar.
   d. Two zincs plus two hydrochloric acids plus two chlorides will produce hydrogen.
   e. Oxygen has a strong odor; it extinguishes a flame.
   f. Oxygen can be prepared by hydrochloric acid on hydrogen chloride.
   g. Test for carbon dioxide by burning a flint.
   h. Test for carbon monoxide: Canary plus CO equals no canary plus CO.
2.


You sure could use some Scope!
SO_2
O_2

CHEM 13 NEWS, February 1983, p. 14

3. **TWO GAS PUNS**:
   a. Albert the German astronomer goes out tonight to watch the stars. "It must be cloudy," he exclaims, "for I Xenon."
   b. Said Benny the burglar, "It's time that I made another Radon the bank."

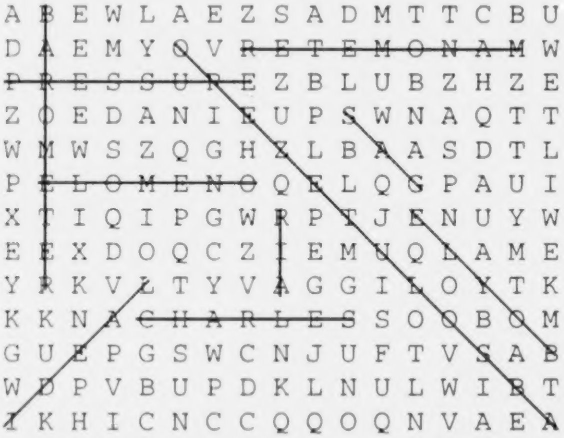
   CHEM 13 NEWS, April 1980, p. 7

4. **BOYLE'S LAW: TWO ANECDOTES**
   a. When stewardesses on commercial planes complained that their skirts fitted on the ground, but not in the air, an airline spokesman blamed it all on Sir Robert Boyle's Law. This law says that if the quantity and temperature of a gas remain constant, its volume will vary inversely with pressure.

      The application of the law to the skirts is simple: Air pressure decreases as an airplane ascends, and thus the pressure on the gas in a stewardess' stomach lessens, which means the volume of the gas increases. In other words, her tummy bulges. Stewardesses now wear adjustable skirts.
   b. During the construction of a tunnel under a river, a party of politicians went down to celebrate the meeting of the two shafts. They drank champagne and were disappointed that it was under depth pressure—the carbon-dioxide bubbles remained in solution. When the town fathers arrived at the surface, the wine popped in their stomachs, distended their vests and all but frothed from their ears. One dignitary had to be rushed back into the depths to undergo champagne recompression.

   CHEM 13 NEWS, March 1973, p. 572

5. Word Search (see *Appendix* for master copy)



A B E W L A E Z S A D M T T C B U
D A E M Y Q V ~~R E T E M O N A M~~ W
~~P R E S S U R E~~ Z B L U B Z H Z E
Z O E D A N I E U P S W N A Q T T
W M W S Z Q G H Z L B A A S D T L
P ~~E L O M E N O~~ Q E L Q G P A U I
X T I Q I P G W R P T J E N U Y W
E E X D O Q C Z I E M U Q L A M E
Y R K V L T Y V A G G I L O Y T K
K K N A ~~C H A R L E S~~ S O O B O M
G U E P G S W C N J U F T V S A B
W D P V B U P D K L N U L W I B T
I K H I C N C C Q Q O Q N V A E A

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Gas whose behavior can be predicted by PV = nRT.
2. Device used to measure the pressure of a gas.
3. State of matter with no definite shape or volume.
4. Gas law that states: V = k/P.

5. Device used to measure atmospheric pressure.
6. 0 K or –273.15 degrees Celsius (2 words)
7. Gas law that states: V = kT
8. This quantity of gas at STP occupies 22.4 L. (2 words)
9. Gaseous mixture of nitrogen, oxygen, and trace gases found in the atmosphere.
10. Force per unit area exerted by a gas in a closed container.

Answers: 1. IDEAL 2. MANOMETER 3. GAS 4. BOYLE 5. BAROMETER 6. ABSOLUTE ZERO 7. CHARLES 8. ONE MOLE 9. AIR 10. PRESSURE

6. See cartoons at end of the module.

MEDIA

1. CHEM Study film and video on gases, *Gases and How They Combine*. Available from Ward's Natural Science Establishment, P.O. Box 92912, Rochester, NY; (800) 962-2660.
2. The Cable Weather Channel periodically runs films on environmental issues that may be taped for class.
3. Software published by *JCE:* Software, a publication of the *Journal of Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).*

   Ideal Gas, by Richard Hiatt, Vol. IV, No. 1, for the Apple II computer.
4. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, Wl 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

   a. For the Apple II computer: AP 401, AP 402, AP 404

   c. For IBM PCs and PC-compatibles: PC 2601, PC 2602, PC 2603
5. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wl 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   "Experimenting with Gas Pressure I," "Experimenting with Gas Pressure II," "Effect of Temperature on Pressure," and "Experimenting with Gas Pressure III," four chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc I (double sided, 60 min.), Special Issue 3.

Links/Connections

WITHIN CHEMISTRY

1. Use of gases in stoichiometry (see *Extensions*).
2. Effect of pressure on changes of state; change of boiling point with change in atmospheric pressure.
3. Determination of molar masses of unknown gaseous substances by researchers.

TO THE CONTEMPORARY WORLD

1. **Acid Rain**. The gases NO_2 and SO_2 contribute to acid rain. These gases dissolve in water droplets or aerosol particles, causing the pH to decrease. This moisture precipitates as acid rain or acid snow. NO_2 produces nitric acid (HNO_3) and nitrous acid (HNO_2); SO_2 produces sulfurous acid (H_2SO_3) and, after conversion to SO_3, sulfuric acid (H_2SO_4). Rain is naturally acidic (pH = 5.6) from the CO_2 gas that dissolves in water to form carbonic acid (H_2CO_3). Acid rain has pH values below 5.6.
2. **Ozone Depletion by Chlorofluorocarbons (CFCs).** CFCs are halogenated hydrocarbons that find use as refrigeration fluids, degreasing solvents for electronic parts, fire extinguishers (CFCs are unreactive) and, at one time, aerosol propellants for hair sprays, deodorants, and food. Their use as propellants is now banned in the U.S. due to evidence that they help destroy the ozone layer. In the stratosphere where ozone is the most abundant, ultraviolet light breaks down CFCs forming a very reactive chlorine atom (Cl). The chlorine atom and an ozone molecule combine producing an oxygen molecule and another reactive atom. A chain reaction occurs consuming many more ozone molecules. The stratospheric ozone layer filters out harmful ultraviolet rays, preventing skin cancer.
3. **Photochemical Smog**. Originally smog meant a combination of smoke and fog. Today it generally refers to the polluted air found over cities as a result of industrial emissions and automotive exhaust. The major chemical substances involved are hydrocarbons (unburned fuel), nitrogen oxides (which form at the high temperatures and pressures of internal combustion engines) and ozone. Ozone production is a light activated reaction and an example of a process contributing to photochemical smog. NO_2 decomposes in light to nitrous oxide and free oxygen. The latter combines with molecular oxygen to make ozone.

$$NO_2 \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$

   The ozone then reacts with various hydrocarbons to produce aldehydes, peroxynitrates, acrolein, and other irritants. These induce health problems in some humans and produce a phytotoxic effect in plants. Even some carcinogens are found in smog. Air pollution problems are aggravated by local geographic conditions in cities such as Denver and Los Angeles. Consequently, gaseous emissions are restricted in these places.

Consequently, gaseous emissions are restricted in these places.

4. **The Greenhouse Effect**. Carbon dioxide is transparent to visible and ultraviolet light but absorbs infrared radiation strongly. As a consequence, the atmosphere of the earth is warmer than it would be without carbon dioxide. Incoming higher energy visible light is absorbed at the surface by pigmented objects and organisms. Some of the absorbed energy is emitted as lower energy infrared radiation that is then trapped in the atmosphere. Water vapor also contributes (and, indeed, is the major contributor) to the effect. This warming process is referred to as the Greenhouse Effect.

   The CO_2 composition of the atmosphere has increased with the combination of fossil fuel use and decreasing forested land acreage. There is much concern that this effect might, or already has begun to, lead to global warming that could have disastrous changes in the size of the polar ice caps and distribution of arable land. Scientists are carefully monitoring this situation, and many individuals and governments are acting to reduce CO_2 emissions.

5. **Radon**. A member of the noble gas family, radon-222 is a product of the uranium decay series and is radioactive. It is a direct result of the decay of radium-226.

   $$^{238}U \rightarrow {}^{226}Ra \rightarrow {}^{222}Rn \rightarrow {}^{206}Pb$$

   Radon-222 is found in soil and rocks. When radon-222 decays it produces alpha particles and several short-lived radioisotopes—all of which are alpha emitters. Since radon is a gas, it can be present in the air one breathes. If it decays while in the lungs (half life of radon-222 is about four days) atoms of Po and Pb (both solid elements) and alpha particles are formed. Although the Po and Pb cause problems, alpha radiation damages lung tissue because of close contact with the tissue. This can result in a higher than normal risk of lung cancer.

6. **Commonly Encountered Gaseous Air Pollutants**

Gaseous Pollutant	**Comment**
SO_2, sulfur dioxide	Related to acid rain
O_3, ozone	Pollutant in lower atmosphere, beneficial in stratosphere
CO, carbon monoxide	From incomplete combustion of gasoline in automobile
NO_2, nitrogen dioxide	From combination of N_2 and O_2 in air, in automobiles; related to acid rain problem
CO_2, carbon dioxide	From burning oil, gasoline, coal, and natural gas
CFCs, chlorofluorocarbons	Believed responsible for depletion of ozone layer
Rn-222, radon	Alpha-emitting gas found in rocks and soil

Extensions

The stoichiometry of chemical reactions involving gases can be interpreted through the relationship between amount and volume. Because the volume of a gas is directly proportional to the amount of gas (in moles), volumes of gases can be used experimentally in place of amounts in stoichiometric problems, if temperature and pressure remain constant.

Example: For the reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

2 volumes of $H_2(g)$ react with 1 volume of $O_2(g)$ to form 2 volumes of $H_2O(g)$. By measuring the volume of water vapor formed, one can determine the volume of H_2 that reacted.

To determine the number of moles or grams of H_2 involved, one would use the general gas law in the form $n = PV/(RT)$.

References

Module developed by Jennifer Hubert, Jane Miller, and Marie Sherman, the Missouri team.

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Good biography.

Davenport, D. A. (1983). How the right Professor Charles went up in the wrong kind of balloon. *ChemMatters, 1*(4), 14-16.

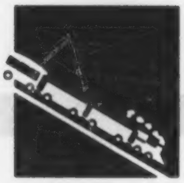
Kuslan, Louis, and Stone, A. (1970). *Robert Boyle.* Englewood Cliffs, NJ: Prentice-Hall, Inc.

Russo, T. (1985, 1986). *Microchemistry for high school general chemistry.*

A pioneer in microscale laboratory methods. Excellent reference.

Sibley, L. K. (1984, October). Popcorn. *ChemMatters, 2*(3), 10-13.

Appendix



- ## Additional Demonstrations

1. Place reagent bottles of concentrated NH_3 and concentrated HCl near each other. Remove both stoppers at the same time and note where the "white smoke" (NH_4Cl) forms. *CAUTION: Handle both reagents with care and avoid breathing vapors.*
2. Environmental
   a. Permanently stretch a rubber band indoors and one outdoors. See how long each takes to deteriorate in the presence of ozone. (The destructive property of ozone was originally discovered due to its action on the rubber coverings of telephone lines.)
   b. Reaction of SO_2 on leaves, stockings, cloth.
   c. To illustrate temperature inversion, rest a 1-L graduated cylinder bottom on an ice bath. Heat cylinder top with lamp. Light a cigarette; drop it into the cylinder.

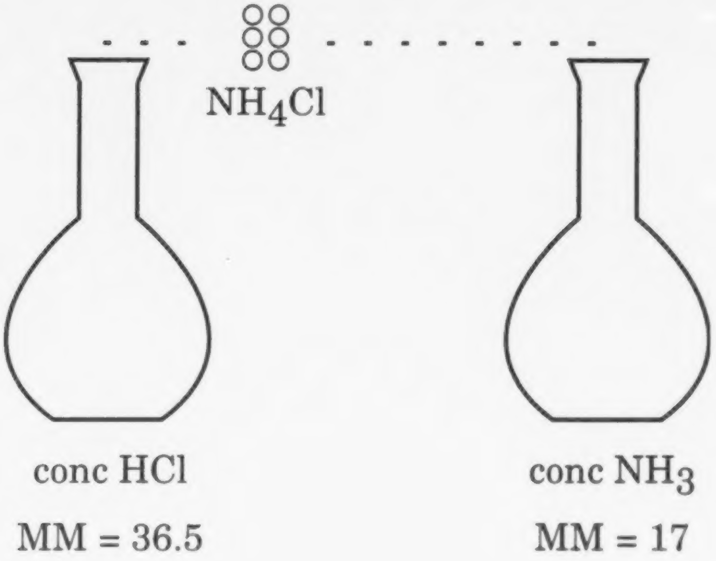
- ## Transparency Masters

1. Formation of Gaseous Ammonium Chloride
2. Effect of Changing Pressure of a Gas on its Volume at Constant Temperature
3. Word Search

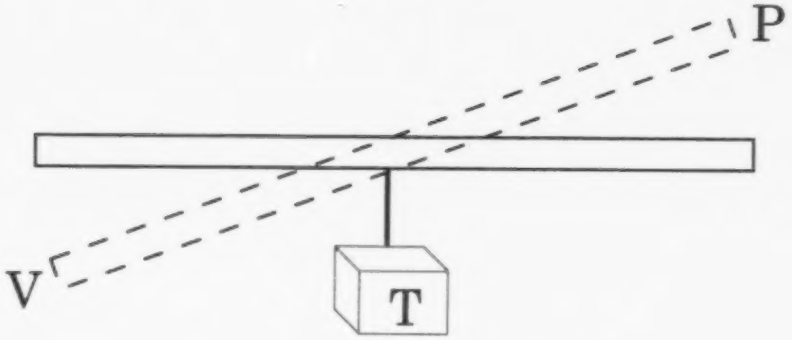
- ## Humor

1. What is this gas?
2. Cartoons

Formation of Gaseous Ammonium Chloride



Effect of Changing Pressure of a Gas on its Volume at Constant Temperature



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Word Search

A	B	E	W	L	A	E	Z	S	A	D	M	T	T	C	B	U
D	A	E	M	Y	O	V	R	E	T	E	M	O	N	A	M	W
P	R	E	S	S	U	R	E	Z	B	L	U	B	Z	H	Z	E
Z	O	E	D	A	N	I	E	U	P	S	W	N	A	Q	T	T
W	M	W	S	Z	Q	G	H	Z	L	B	A	A	S	D	T	L
P	E	L	O	M	E	N	O	Q	E	L	Q	G	P	A	U	I
X	T	I	Q	I	P	G	W	R	P	T	J	E	N	U	Y	W
E	E	X	D	O	Q	C	Z	I	E	M	U	Q	L	A	M	E
Y	R	K	V	L	T	Y	V	A	G	G	I	L	O	Y	T	K
K	K	N	A	C	H	A	R	L	E	S	S	O	O	B	O	M
G	U	E	P	G	S	W	C	N	J	U	F	T	V	S	A	B
W	D	P	V	B	U	P	D	K	L	N	U	L	W	I	B	T
I	K	H	I	C	N	C	C	Q	Q	O	Q	N	V	A	E	A

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3. State of matter with no definite shape or volume.
4. Gas law that states: $V = k/P$.
5. Device used to measure atmospheric pressure.
6. 0 K or –273.15 degrees Celsius (2 words)
7. Gas law that states: $V = kT$
8. This quantity of gas at STP occupies 22.4 L. (2 words)
9. Gaseous mixture of nitrogen, oxygen, and trace gases found in the atmosphere.
10. Force per unit area exerted by a gas in a closed container.

What is this gas?

This gas is very toxic and an extreme fire hazard. It is fatal in concentrations of 0.000001 ppm. Organisms exposed to these gas concentrations die within a few minutes. Symptoms resemble those of cyanide poisoning (blue face, *etc.*). In higher concentration, *e.g.*, about 20%, the toxic effect is delayed, and it takes about 2.5 billion inhalations before death takes place. The reason for the delay is the different mechanism of the toxic effect of this gas in 20% concentration. It apparently contributes to a complex process called aging, of which very little is known, except that it is always fatal.

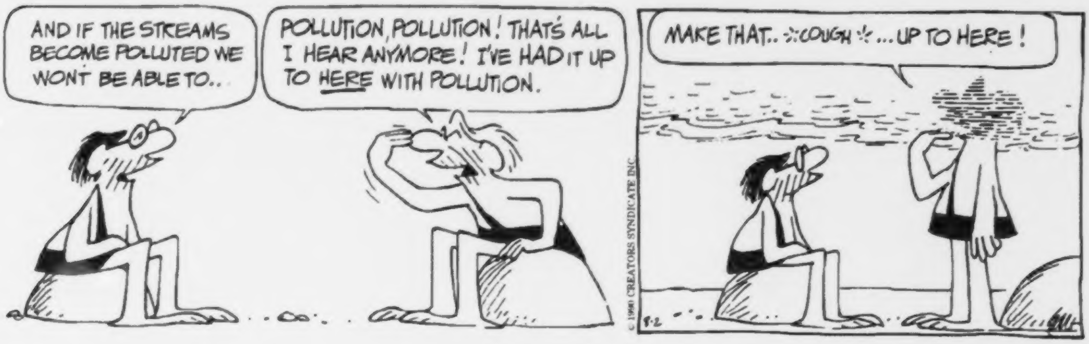
However, the main disadvantage of this 20% gas concentration is the fact that it is habit forming. The first inhalation (occurring at birth) is sufficient to make this gas addiction permanent. After that, any considerable decrease in the daily doses of this gas results in death.

Concentrations higher than 20% decrease the above-mentioned delay. High concentrations of this gas provokes a condition known as retrolental fibroplasia in prematurely born babies placed in incubators. This condition results in blindness. Lung irritation has been reported on experimental animals exposed to high concentrations of this gas for several days.

This gas is an extreme fire hazard. All the fires that were reported in continental U.S. for the period of the past 25 years were attributed to the presence of this gas in the atmosphere surrounding the fire areas.

This gas is especially dangerous because it is odorless, colorless, and tasteless, so its presence cannot be readily detected until it is too late.

The gas described here is oxygen!


AND IF THE STREAMS BECOME POLLUTED WE WON'T BE ABLE TO..
POLLUTION, POLLUTION! THAT'S ALL I HEAR ANYMORE! I'VE HAD IT UP TO HERE WITH POLLUTION.
MAKE THAT.. *COUGH* ... UP TO HERE!
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8-2

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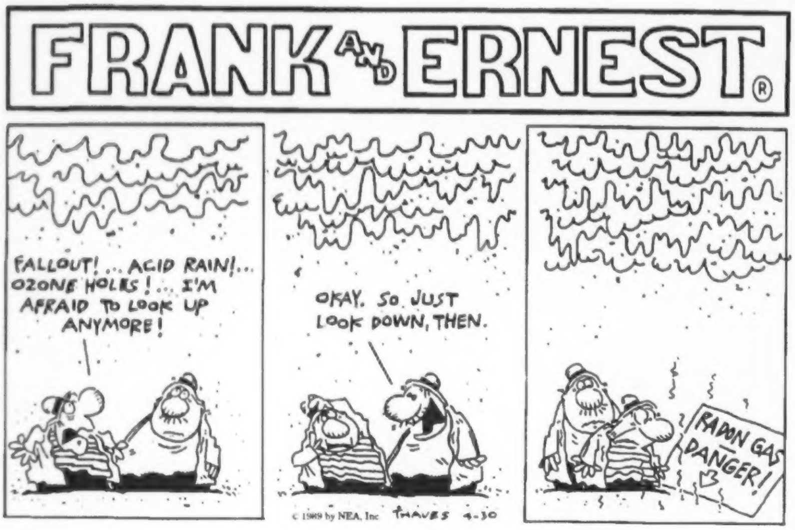
Yes, I know you two have the two lowest atomic numbers and that the Other elements pick on you, but I expect better of you! For Pete's Sake, Helium! You're a noble gas, let's start acting like one, shall we?
H
He

CHEM 13 NEWS, May 1988, p. 1. Reprinted with permission.


FRANK AND ERNEST®
FALLOUT! ... ACID RAIN! ... OZONE HOLES! ... I'M AFRAID TO LOOK UP ANYMORE!
OKAY. SO JUST LOOK DOWN, THEN.
RADON GAS DANGER!
© 1989 by NEA, Inc
THAVES 4-30

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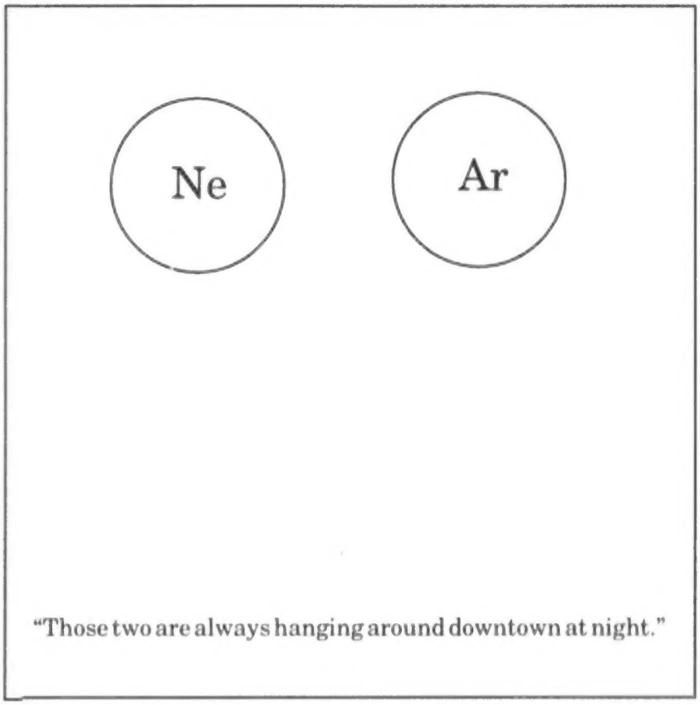

"Those two are always hanging around downtown at night."

© John Ihde, Wausau West High School, Wausau, WI 54401.
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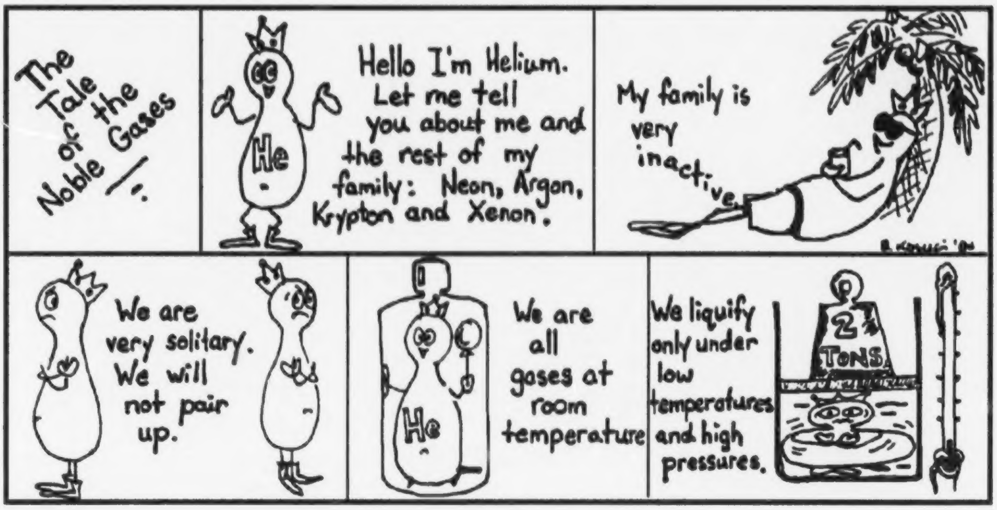
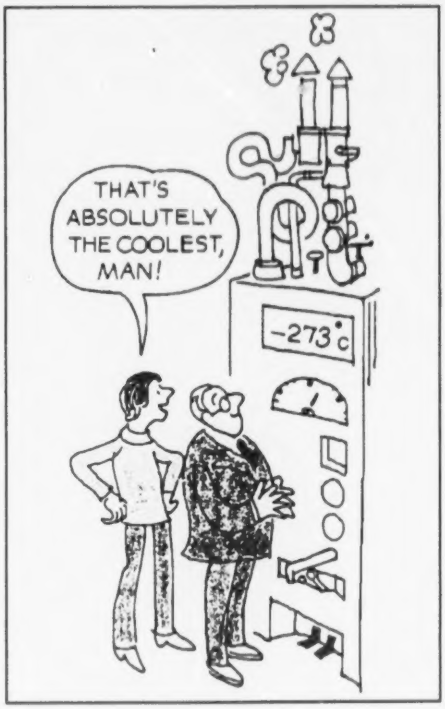

The Tale of the Noble Gases
Hello I'm Helium. Let me tell you about me and the rest of my family: Neon, Argon, Krypton and Xenon.
He
My family is very inactive.
We are very solitary. We will not pair up.
We are all gases at room temperature
He
We liquify only under low temperatures and high pressures.
2 TONS

CHEM 13 NEWS, December 1984, p. 3. Reprinted with permission.

TO OBSERVE AN ODOR, DO NOT HOLD YOUR FACE DIRECTLY OVER THE CHEMICAL. FAN A SMALL AMOUNT TO YOU FROM A DISTANCE.

CHEM 13 NEWS, May and September 1985, p. 25. Reprinted with permission.


THAT'S ABSOLUTELY THE COOLEST, MAN!
-273°C

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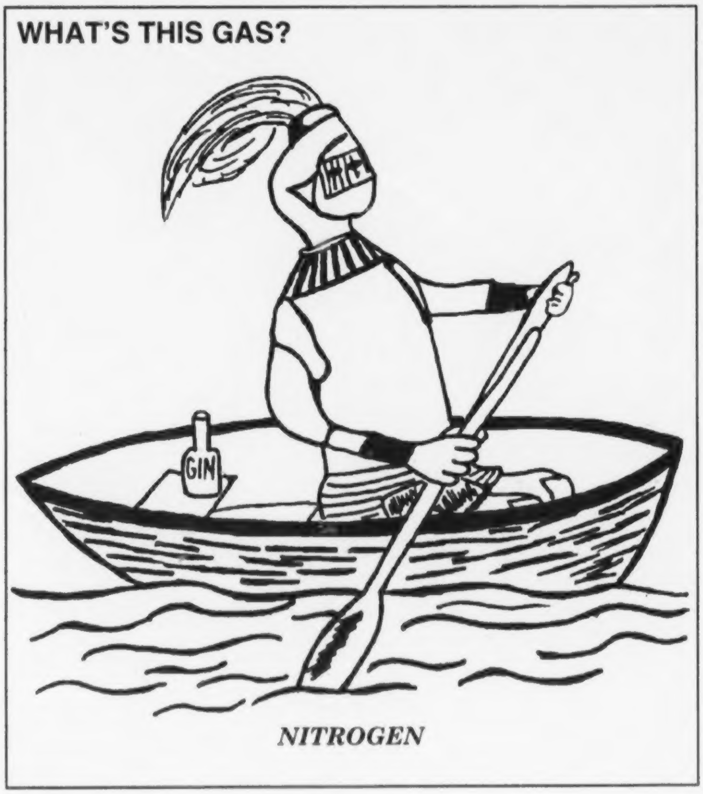

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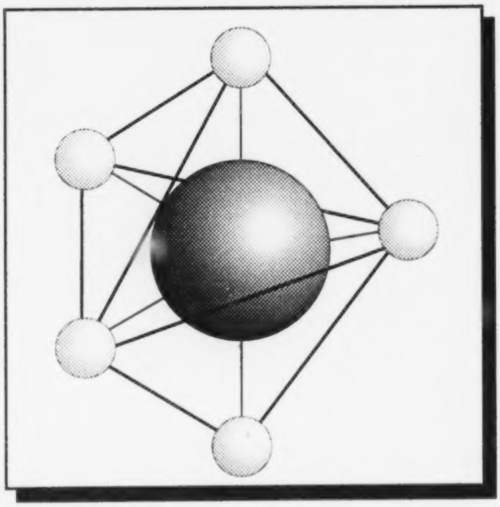
MOLECULAR GEOMETRY



ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

One outstanding accomplishment of quantum mechanical theory is its success in the treatment of molecular geometry. The theory allows prediction of the directional nature of covalent bonds. Although there are many ways to handle molecular stereochemistry, the one discussed in this module is the simplest. It does not involve consideration of hybrid orbitals as in valence bond theory, nor molecular orbitals as in molecular orbital theory. The key to treating molecular geometry is understanding the spatial arrangement of atoms or groups of atoms relative to the central atom(s) in a molecule or ion through bonds with a substantial degree of covalent character.

The stereochemistry of molecules refers to the three-dimensional geometric arrangement of atoms or groups around a central atom(s). The molecular shapes are named according to the geometric shapes of the solid figures defined by the bonds between the central atom and the atoms attached to it. The most common shapes are linear, bent, trigonal planar, trigonal pyramidal, square pyramidal, tetrahedral, trigonal bipyramidal, and octahedral. Experimental methods for determining structure are diffraction methods (X-ray, electron, and neutron diffraction), spectroscopic methods (infrared, microwave, visible, ultraviolet, and Raman), resonance methods (nuclear magnetic and electron paramagnetic), and physical methods such as dipole moment and magnetic susceptibility determinations. These methods will not be considered in this module.

N. Sidgwick and H. Powell, in 1940, developed the foundation for a new, simplified theory of the stereochemistry of molecules. Based upon a survey of the then known inorganic compounds, they suggested that the electron pairs in the valence shell of a polyvalent atom (capable of forming more than one covalent bond) are always arranged in a way so as to minimize the repulsions between them. This arrangement applies to both bonding pairs (shared pairs) or nonbonding pairs (unshared or lone pairs) of electrons. Thus, two electron pairs will arrange linearly, three pairs as a planar triangle, four pairs tetrahedrally, five pairs as a trigonal bipyramid, and six pairs octahedrally. This simple theory is capable of predicting the shape of all known compounds of representative elements for which the valence shell electron pairs are all bonded to identical atoms or groups. If one or more electron pairs are unshared, or if there are two or more different kinds of bonded atoms, deviations from the regular structures are expected.

This theory of the stereochemistry of molecules is now called the Valence Shell Electron Pair Repulsion theory and is usually referred to by its acronym VSEPR. VSEPR became popular after Gillespie published an article about it in the *Journal of Chemical Education* in 1963 [Gillespie, R. J. (1963). *Journal of Chemical Education, 40,* 295]. Today it is the theory of choice in most high school chemistry texts and ranks high in college general chemistry texts. Valence bond theory, which invokes the use of hybrid orbitals, is another popular theory discussed in most textbooks.

The shape and polarity of molecules determine the type of intermolecular interaction, which, in turn, determines the properties of molecules. Generally, molecular species have low melting and boiling points, are relatively soft, may form acids or bases in solution, and are soluble or insoluble depending upon their polarity and the nature of the solvent.

PLACE IN THE CURRICULUM

Molecular geometry logically follows development of the covalent bond concept. Most chemistry teachers prefer introducing it along with or immediately after covalent bonding and polar covalent bonding. Personal preference or the organization of the student textbook may well dictate its placement. In any case, students first need to be able to write Lewis-dot structures, have an understanding of electrostatic forces, polar and nonpolar covalent bonds, and some knowledge of elementary geometric shapes.

CENTRAL CONCEPTS

1. The geometric shape of a molecule can be predicted by focusing attention on the structure's central atom(s) and the mutually repulsive valence shell electron pairs surrounding it. This approach is known as the valence shell electron pair repulsion (VSEPR) approach.
2. Two kinds of valence electron pairs may populate the central atom(s) of a molecule—bonding pairs and nonbonding pairs (lone pairs). Repulsions between adjacent pairs of electrons vary in strength depending upon whether they are bond pair-bond pair (BP-BP), bond pair-lone pair (BP-LP), or lone pair-lone pair (LP-LP). The repulsion order is considered to be:

   $$\text{BP-BP} < \text{BP-LP} < \text{LP-LP}$$

   This concept helps explain the spatial distribution of electron pairs; lone pairs spontaneously arrange themselves to be as far apart as possible, bond pair-lone pairs are next, and bond pair-bond pairs are found to be the closest.
3. In the VSEPR approach, electron pairs on the central atom(s) are viewed as assuming positions around that atom that minimize electron pair-electron pair repulsions. The resulting electron pair geometry about the central atom determines the placement of the atoms bonded to the central atom(s). The resulting arrangement of bonded atoms determines the molecular geometry.
4. Molecular geometries may be classified according to the number of lone pairs and bonding pairs of electrons surrounding the central atom—*e.g.*, two bonding pairs = linear; three bonding pairs = trigonal planar; two bonding pairs and one lone pair = angular (bent); and so forth.
5. Molecules containing one or more polar covalent bonds may either be polar or nonpolar, based on the extent of the bond polarities and molecular geometry.
6. The shape and polarity (or lack of polarity) of a given molecule help determine the general properties of the substance composed of these molecules.

RELATED CONCEPTS

Electrostatic attraction and repulsion form the basis for the bonding considered in this module; therefore, students should know that like charges repel, unlike charges attract, and electrostatic forces decrease as the inverse of the square of the separating distance.

RELATED SKILLS

1. Students should be proficient at writing Lewis-dot structures of simple molecules. Check to determine whether students have retained this skill. Reteach if students are not proficient at writing Lewis-dot formulas for the kinds of molecules that are used here.
2. To visualize molecular shapes, it is necessary to be able to create three-dimensional "pictures in the mind." Molecular models help immeasurably with this skill and should be liberally used by both student and teacher.

PERFORMANCE OBJECTIVES

After completing their study of molecular geometry, students should be able to:

1. use appropriate materials to build adequate models of simple molecules and polyatomic ions representing the shapes of these species.
2. recognize the utility of using VSEPR theory as a predictive device and use it to predict shapes of simple molecules and polyatomic ions.
3. recognize that names given to shapes of molecular and polyatomic ionic species reflect geometric shapes of polygons that would contain the species when the edge lengths are appropriate.
4. appreciate the beauty and symmetry inherent in molecular shapes.
5. use a knowledge of molecular geometry to help link topics in chemistry, related fields, societal needs and problems.
6. predict the polarity of a molecule given its shape and types of bonds.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Building Molecular Models

Introduction

Most molecules in this activity obey the octet rule. Their Lewis-dot structures are straightforward. Recall that to draw the Lewis-dot structure of a molecule obeying the octet rule, eight electrons on each atom (except hydrogen and a few others) are arranged in four pairs. Each pair either participates in a covalent bond or is present as a lone pair. Some molecules may have an odd number of valence electrons or may have more than four pairs on the central atom. If any of these are encountered, your teacher will provide the necessary information.

According to the electron pair repulsion rule, the regions of high electron density (two, three, or four electron pairs) around an atom move as far apart as possible without leaving the atom. Double and triple covalent bonds are treated as a single electron pair or region of high electron density determing molecular shape. Lone pairs are considered when determing electron distribution, but only the geometric distribution of atoms dictates molecular shape.

When four electron pairs around a central atom form single bonds, the pairs can be arranged tetrahedrally. This arrangement assures that the electron pairs are as far apart as possible, satisfying the pair repulsion rule. Three electron pairs can be arranged to form a triangular plane, two to form a straight line, *etc.*

Molecular shape is determined by the positions of the atoms in a molecule, not the electrons. For a central atom with four tetrahedrally arranged electron pairs, bonding to four other atoms will yield a molecule with tetrahedral geometry; bonding to three other atoms results in a triangular pyramid with one lone pair, and bonding to two other atoms yields a bent shape with two lone pairs.

The following table summarizes these ideas.

Electron pairs	Bond pairs	Lone pairs	Example	Angle	Shape
4	4	0	CCl_4	109.5°	Tetrahedral
4	3	1	PCl_3	<109.5°	Pyramidal
4	2	2	SCl_2	<109.5°	Bent
3	3	0	BCl_3	120°	Triangular
3	2	1	$SnCl_2$	<120°	Bent
2	2	0	$BeCl_2$	180°	Linear

Remember that the "repulsive effect" of a double or triple bond is counted the same as that of a single electron pair.

Knowing the geometry of a molecule allows one to predict whether it is polar or nonpolar. A bond between unlike atoms is usually polar with a positive end and a negative end. The symmetry of the molecule determines polarity. Formal rules are available for this determination, but the easiest way for beginning chemistry students is to decide whether each polar bond is countered by another identical bond in the molecule.

A diatomic molecule containing two different atoms is polar. Examples are HF, CO, and ICl. N_2 and O_2 are nonpolar since both ends of the molecules are equivalent. A polyatomic molecule may be nonpolar even if it contains polar bonds because, in such cases, the polar bonds are counteracting each other. CO_2 and CH_4 are nonpolar because of this geometric (symmetrical arrangement) effect.

Ball-and-stick models will be used to represent the shapes of molecules in this activity. Several molecular models will be built. The molecular formulas, the Lewis-dot structures, sketches of the molecules, the names of the molecular shapes, the approximate bond angles, and the polarities will be recorded in a data table.

Purpose

To predict shapes, bond angles, and polarities of some molecules and to build models of these molecules confirming the predictions.

Safety

There are no unusual hazards in this activity.

Procedure

1. Construct a data table having eight columns with headings as follows: molecular formula, Lewis-dot structure, number of bond pairs, number of lone pairs, molecule sketch, molecular shape, bond angle, and polarity. Use the page's long axis for the column labels. Record data for each of the assigned molecules in the data table as the procedure is followed.
2. Write the molecular formula, and draw the Lewis-dot structure for each of the following molecules: CH_4, H_3O^+, N_2, C_2H_2, CH_2Cl_2, HF, Cl_2, SO_2, CH_4O, NH_3, C_2H_4, SO_4^{2-}, H_2, H_2O_2, CH_2O, CO_2.

   The formula should be in the first column and the Lewis-dot structure in the second column.
3. Using ball-and-stick models, build a model for each of the assigned molecules after completing Step 2 above. After completing each model, take it to your teacher to be checked. Draw a sketch of each model as soon as it is checked; then complete the remaining five entries in the data table.
4. After completing your table, your teacher will give you formulas for two unfamiliar molecules. Predict the shape, bond angle, and polarity after recording the formula and the Lewis-dot structure. Take your data table to your teacher to be initialed.
5. After your teacher has initialed your predictions, build the models to confirm them.
6. Return the model sets as your teacher directs.

Data Analysis

1. Did your prediction of the geometry of the unknowns prove valid? Why or why not?
2. Did your prediction of the polarity of the unknowns prove valid? Why or why not?

Implications and Applications

1. CO_2 is nonpolar, but SO_2 is polar. Explain.
2. Describe the electronic similarities between NH_3 and H_3O^+. These species are called isoelectronic. Why?
3. Using your data table try to write some rules of thumb that would allow predictions of molecular geometry. These rules of thumb are generalizations and should include the total number of electron pairs, the number of bonding pairs, and the number of lone pairs on the central atom. Develop a table having columns containing number of electron pairs, number of bond pairs, number of lone pairs, molecular shape, and an example. The table should summarize the rules of thumb.
4. Develop some rules of thumb to help with determining molecular polarity. These rules should be in terms of the shape of the molecule and the kinds of atoms bonded to the central atom (all alike or some different, *etc.*).
5. Relate the Lewis-dot structure to the geometry of molecules.

Reference

Doing Chemistry. (1988). Washington, DC: American Chemical Society.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Building Molecular Models

Major Chemical Concept

This activity should provide the student with additional practice in drawing Lewis-dot structures, predicting molecular shapes from these drawings using the VSEPR model, and then constructing models of these molecules using appropriate modeling materials (*e.g.*, ball-and-stick kits, or Styrofoam® spheres of various sizes and colors. Gum drops and tooth picks may be used if other materials are not available.)

Level

This activity may be used for students at all ability levels. With basic students use only simple molecules such as NH_3, H_2O, *etc.* The general student should be able to use more complex molecules at least through the tetrahedral case such as CH_4, including polyatomic ions like SO_4^{2-}, and some simple two-center molecules such as C_2H_2 and H_2O_2. For the honor students all cases may be treated.

Expected Student Background

Students should be familiar with writing Lewis-dot structures and applying the octet rule. They should recognize simple geometric shapes such as the triangle, tetrahedron, trigonal pyramid (square, trigonal bipyramid, square-based pyramid, octahedron, *etc.*, if more complex molecules and ions are included). Finally, it is assumed that—at minimum—covalent bonding (including polar bonding) has been taught.

Time

Teacher preparation time is very short—about 5-10 min to set out the molecular model kits. Students should be able to finish the activity in 40-50 min. It should only require 5-10 min to complete the unknowns.

Safety

Read the *Safety Considerations* in the *Student Version*. There are no unusual hazards in this activity. Remind students not to throw, roll, or otherwise damage the models, and to follow routine laboratory precautions.

Materials (For 24 students working in pairs)

If ball-and-stick models are used, one set per student pair is required. If Styrofoam® spheres are used, it is recommended that the denser type of spheres be used since they last longer.

96 Styrofoam® spheres, 3-in
180 Styrofoam® spheres, 2-in
240 Pipe cleaner sections about 1-in long (or toothpicks)
12 Drawing compasses
12 Metric/English scale rulers

Advance Preparation

If ball-and-stick models will be used, you should make all of the models in the activity to see what is involved for the student. It is also valuable to have a reference set available for students. It would be helpful to have solid models (made of poster board, old manila folders or construction paper) of the common geometric shapes ascribed to molecules.

Make a list of "unknown" molecules to assign to students after they have completed the assigned list. The unknowns should consist of molecules similar to those used for the experimental procedure. For example, instead of H_2O, OF_2 could be used as an unknown. Make models of the unknowns to check for "impossible" ones. The unknowns should be easily predicted and constructed, particularly for the general and basic students.

Although ball-and-stick models are ideal for this activity, it is possible to have students build models from expanded polystyrene spheres. It is more difficult and time consuming, but not impossible. The following is a suggested procedure for this purpose.

Show students how to mark-off a sphere for the tetrahedral shape. If *Doing Chemistry* is available, use a video sequence from the videodisc B17391 to show how this may be done. The following description provides the needed steps.

Plane geometry allows one to calculate that the distance between any two tetrahedral points on the surface of a sphere is given by 0.82 D, where D is the sphere's diameter. Mark any single point on the sphere. Set a compass to 0.82 D for the diameter of the Styrofoam® sphere. The compass must be tight and able to hold the 0.82 D distance. Place the compass point at the marked point and draw a circle on the sphere having 0.82 D diameter. Mark a second point on the previously drawn circle, place the compass point there, and with the same compass setting mark two additional points on the circle. This gives four points on the sphere. Hold the sphere so that a point is at the top. Insert a toothpick vertically into the point. Then add toothpicks at the remaining three points in the same fashion. The bonds (toothpicks) should all be at the tetrahedral angle from each other.

Triangular planar templates made from cardboard should be provided. Draw an equilateral triangle large enough so that the size spheres used fit comfortably in the center. Draw a perpendicular line to each side of the triangle from the opposite vertices. The three lines should mark the center of the triangle. Using a compass set to the diameter of the sphere, place its point at the center of the triangle, draw a circle and cut it out. The spheres should now fit into the hole with the lines from the vertexes showing where toothpick bonds are to be placed (see Figure 1).

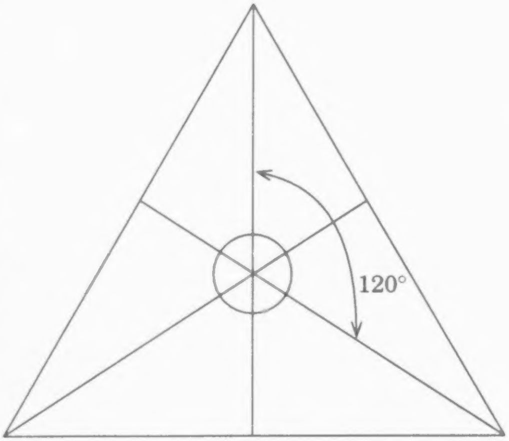


Figure 1. Template for trigonal planar model.

Students may use these templates to help them construct models from Styrofoam® spheres with correct angular relationships.

Pre-Laboratory Discussion

Prior to having students build models, assign the task of completing Lewis-dot structures as homework the night before the laboratory. Briefly review drawing these structures. The Pauling-Giddings method (see *Chemical Bonding* module) is a quick and convenient way of determining how many bonds are on the central atom. The Lewis-dot structure is then easily drawn.

Demonstrate the method of making a tetrahedral template. Also show how the triangular templates are used.

If students are to use ball-and-stick models, demonstrate the correct manner of putting them together. In particular, point out that the sticks should not be jammed into the balls so tightly that removal is difficult. Show that for two center molecules, longer sticks should be used for C—C bonds and shorter ones for other bonds. Also show how springs are used to represent multiple bonds. Point out that springs are useful models for bonds since they stretch and bend as do chemical bonds. However, double and triple bonds restrict rotation between two adjacent bonded atoms. (A short piece of rubber tubing is helpful in removing jammed pegs when disassembling.)

Help students organize a data table. A simple format is shown here. Remember that there will be as many rows as there are molecules and ions plus an additional one for each unknown.

Shapes of Covalent Molecules

Molecular formula	Lewis-dot formula	# Bond pairs	# Lone pairs	Ball/Stick model	Shape	Bond angle	Molecular polarity
CH_4							
CH_2Cl_2							

The choice of which molecules and ions to have students model is critical. The ones given in the procedure section are suitable for general students. Some molecules may be too complex for basic students, and honor students probably need more challenge than that provided by this set. To provide more options, two additional listings are given. The first does not include molecules or ions having trigonal bipyramidal or octahedral central atoms. The second includes molecules and ions that do have trigonal bipyramidal and octahedral centers. If ordinary ball-and-stick models or Styrofoam® models are used, the models students can build will be restricted. Some ball-and-stick sets do have trigonal bipyramidal and octahedral centers. The choice of molecules and ions will depend upon what modeling material is available.

Molecules and Ions for Kits *not Having* Trigonal Bipyramidal and Octahedral Centers

Set A: CH_4, NH_3, NO_3^-, H_2S, C_2H_2, CO_2, C_2H_6, C_2H_4, BCl_3, C_4H_{10}

Set B: $CHCl_3$, PCl_3, NH_4^+, O_3, HCO_3^-, N_3^-, SF_2, C_2F_4, C_4H_{10}, SO_3^{2-}

Set C: CCl_4, ClO_3^-, H_3O^+, SO_2, C_2Cl_4, SCN^-, $C_3H_6Cl_2$, Cl_2O, BF_3, CO_3^{2-}

Set D: CH_2Cl_2, PH_3, ClO_4^-, $HOCl$, NH_2OH, SiO_2, $C_2Cl_2F_2$, CH_3OCH_3, B_2H_4, SO_3

These sets may also be used as sources of unknowns for the activity. Exercise judgment about which of these you assign to students, particularly some of the two- and three-center species. The idea for using unknowns is that the unknowns are within the ability of the student. Ions, other than simple ones, may prove difficult for the general student.

Molecules and Ions for Kits *Having* Trigonal Bipyramidal and Octahedral Centers

Set A: CH_4, B_2H_4, NCl_3, H_3O^+, PCl_5, CO_3^{2-}, CS_2, ICl_4^-, H_2S, C_4H_{10}

Set B: $CHCl_3$, BF_3, ClO_3^-, NH_4^+, I_3^-, SO_3^{2-}, C_2H_2, IF_5, $HOCl$, $C_3H_6Cl_2$

Set C: CCl_4, CH_2O, BrO_3^-, PO_4^{3-}, ClF_3, NO_3^-, SCN^-, SF_6, SO_2, $C_2H_2F_2$

Set D: CH_2Cl_2, $S_2O_3^{2-}$, PH_3, ClO_4^-, ICl_3, HCO_3^-, SiO_2, SiF_6^{2-}, O_3, $C_2H_3Cl_3$

The sets having trigonal bipyramid and octahedral shaped species should prove more challenging and useful for honor students.

Teacher-Student Interaction

Have students bring the models to you one at a time. Grade each one individually. If the first model is incorrect, give the student a second chance to complete the structure successfully. Mark students' data tables when they bring a correct model. It is highly desirable to have a complete model set available to show students the correct shapes. This immediate reinforcement should be helpful.

When students are completing their unknowns, circulate and give them hints. You may wish to use the unknowns to assess laboratory learning.

Anticipated Student Results

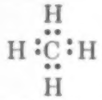
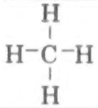
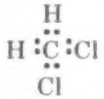
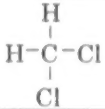
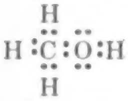
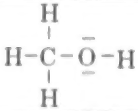
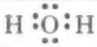
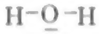
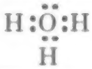
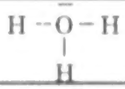
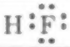
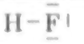
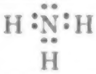
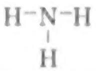
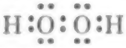
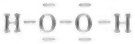
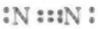
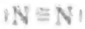
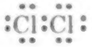
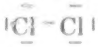
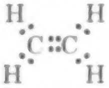
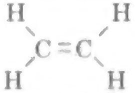
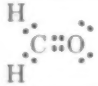
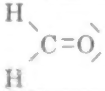
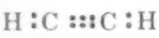
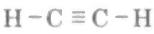
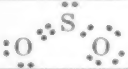
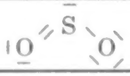
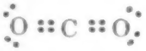
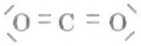
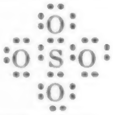
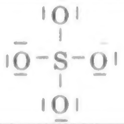
The following sample data table shows anticipated student results.

Student answers to questions asked in the data analysis section will vary. It is anticipated that most students will be successful in completing the table, particularly after receiving help during the course of the activity. More difficulty will be encountered with predicting molecular polarity than the other parts of the procedure. Students should give some reason why the predictions were either valid or invalid.

Answers to Implications and Applications

1. CO_2 has only two regions of high electron density and both are due to two electron pairs (double bonds). Since there are only two electron pairs determining the geometry, they will lie on a line on opposite sides of the central carbon atom. The result is a symmetrical linear model that is nonpolar. In the case of SO_2, there are three regions of high electron density; a single bond, a double bond, and a nonbonding pair of electrons. The three regions of electron density force a bent shape on the molecule since the nonbonding pair repels more strongly than do the bond pairs. The bent shape gives rise to a polar molecule.
2. Electronically, NH_3 and H_3O^+ are identical. In such cases structures are called **isoelectronic** meaning there are equal numbers of valence electrons in both.
3. Possible Rules of Thumb for predicting molecular shapes: (*NOTE: You will probably need to help students devise rules of thumb.*) Determine the number of valence electron pairs, number of bond pairs, and number of nonbonding pairs (lone pairs) through Lewis-dot structures or the Pauling-Giddings Rule (see *Chemical Bonding* module). It is convenient to represent these cases with general formulas having *A* representing the central atom, *X* representing the attached atoms, and *E* representing lone pairs of electrons. (Students may not be able to develop these; you may have to provide this information.)

   Case 1. Two electron pairs total with two bond pairs and no lone pairs predicts a linear structure. AX_2

Molecular formula	Lewis-dot formula	# Bond pairs	# Lone pairs	Ball/Stick model	Shape	Bond angle	Molecular polarity
CH_4		4	0		Tetrahedral	109.5°	Nonpolar
CH_2Cl_2		4	0		Tetrahedral	109.5°	Polar
CH_4O		4(C) 2(O)	0(C) 2(O)		Tetrahedral at C	109.5°	Polar
H_2O		2	2		Bent	109.5°	Polar
H_3O^+		2	2		Pyramidal	109.5°	Polar
HF		1	3		Linear	180°	Polar
NH_3		3	1		Pyramidal	109.5°	Polar
H_2O_2		2 Each	2 Each		Bent	109.5°	Polar
N_2		1 Each	1 Each		Linear	180°	Nonpolar
Cl_2		1 Each	3 Each		Linear	180°	Nonpolar
C_2H_4		3 Each	0 Each		Planar	120°	Nonpolar
CH_2O		3 Each	0(C) 2(O)		Planar	120°	Polar
C_2H_2		2 Each	0 Each		Linear	180°	Nonpolar
SO_2		3(S)	1(S)		Bent	120°	Polar
CO_2		2(C) 1(O) Each	0(C) 2(O) Each		Linear	180°	Nonpolar
SO_4^{2-}		4(S) 1(O) Each	0(S) 3(O) Each		Tetrahedral	109.5°	Nonpolar

Case 2. Three electron pairs total with three bond pairs and no lone pairs predicts a triangular planar (or trigonal planar) structure. AX_3.

Case 3. Three electron pairs total with two bond pairs and one lone pair predicts a bent (or angular) structure. AX_2E.

Case 4. Four electron pairs total with four bond pairs and no lone pairs predicts a tetrahedral structure. AX_4.

Case 5. Four electron pairs total with three bond pairs and one lone pair predicts a trigonal pyramidal structure. AX_3E.

Case 6 Four electron pairs total with two bond pairs and two lone pairs predicts a bent structure. AX_2E_2.

Case 7. Four electron pairs total with one bond pair and three lone pairs predicts a linear structure. (This is a trivial case since with only two atoms present, the resulting structure must be linear.) AXE_3.

4. Possible Rules of Thumb to predict molecular polarity. *(NOTE: You will probably need to help students develop these rules of thumb.)*

Determine whether polar bonds are present by calculating the electronegativity difference between the two atoms. If no, then the molecule must be nonpolar. If yes, the molecule *may* be polar.

Case 1. Linear molecules with identical atoms attached to the central atom will always be nonpolar, *e.g.*, BeF_2.

Case 2. Triangular planar molecules with identical atoms attached to the central atom will always be nonpolar, *e.g.*, BCl_3.

Case 3. Bent molecules with two bond pairs and one lone pair will always be polar, *e.g.*, $SnCl_2$.

Case 4. Tetrahedral molecules with four bond pairs and with four identical atoms bonded to the central atom will be nonpolar, *e.g.*, CCl_4. If one, two, or three of the bonded atoms are different from the others, the molecule will be polar, *e.g.*, $CHCl_3$.

Case 5. Trigonal pyramidal molecules with three bond pairs and one lone pair will be polar, *e.g.*, NH_3.

Case 6. Bent molecules with two bond pairs and two lone pairs will be polar, *e.g.*, OF_2.

Case 7. Linear molecules with one bond pair and three lone pairs will be polar, *e.g.*, HCl.

5. The Lewis-dot structure provides the number of electron pairs surrounding the central atom making it possible to determine the number of bond pairs and lone pairs. This information is needed to predict the molecular structure.

Post-Laboratory Discussion

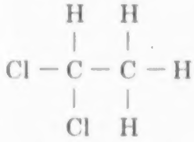
During the post-laboratory discussion, concentrate on helping students develop and apply the rules of thumb. These rules are not necessarily obvious, so have a "generic set" of molecular shapes available to use with the discussion. Model sets should also be available so students can construct the models and better follow development of the VSEPR concept. This exercise should serve well as a major teaching activity for the module.

A generic set of molecular models may be constructed from 1- and 2-in polystyrene spheres, 1/8-in dowels, and some glue. These models prove helpful in demonstrating the shapes being considered.

One point that should be made in post-laboratory discussion is that the shapes shown by the models are idealized. Actual molecules deviate somewhat from the ideal shapes, particularly if there are different kinds of atoms bonded to the central atom (as in $CHCl_3$). A distorted tetrahedron would be the result since the hydrogen atom is smaller than the chlorine atoms.

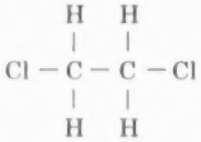
Extensions

1. For some molecules with a given molecular structure it is possible to satisfy the octet rule with two, three, or more arrangements of the atoms. For example, it is possible to draw two different Lewis-dot structures for $C_2H_4Cl_2$.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ Cl & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & H & & \end{array}$$

and



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ Cl & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

   In the first case both chlorine atoms are bonded to the same carbon atom, while in the latter case one chlorine atom is bonded to each carbon atom. Since there is free rotation about the C—C bond, the other three bonding positions on each C atom are equivalent. Such molecules with the same formula but different atomic arrangements are called isomers (see *Organic Chemistry* module). Find all the isomers of $C_2H_2Cl_2$. Draw the Lewis-dot structure, build the model, and describe the geometry and polarity of each isomer (three are possible). Note that the double bond between carbon atoms prevents free rotation, making the other bonding positions on the carbon atoms nonequivalent. These structural isomers are important in organic chemistry.

2. Stereoisomerism is another type of isomerism. Draw the Lewis-dot structures, build the models, and describe the geometry and polarity of each isomer of bromochlorofluoromethane, CHBrClF. If necessary, use a mirror with the first model you build to see how to build the second. Note that the difference is the same as the difference between your left hand and right hand; the structures are mirror images of each other. Stereoisomers displaying the phenomenon of "handedness" are important in organic and biochemistry.

3. It is possible for the same structure to have two or more different conformations. Different arrangements of atoms and groups in a molecule are possible as a consequence of rotation about single bonds. For example, cyclohexane, C_6H_{12}, exists in two conformations, the chair conformation and the boat conformation. Build a ball-and-stick model of cyclohexane (a ring compound) and try to form the two conformations. The difference is best seen when the models are viewed from the side (for honor students).

Assessing Laboratory Learning

1. The unknown given to students is a good way to assess laboratory learning. Students who are successful have probably learned what was intended, provided that all unknowns are equally difficult. Assigning unknowns to be built from model kits can also be done after students have completed the activity as a form of "laboratory practical" test. Students should be required to draw the Lewis-dot structure, predict the shape and polarity, and then confirm the shape by building a model.

2. Students can be given several molecules or ions and asked to draw the Lewis-dot structures and to predict the shape and polarity as a paper and pencil test. In this type of assessment, both molecular and ionic species should be used.

DEMONSTRATIONS

CAUTION: Use appropriate safety guidelines in performing demonstrations.

Demonstration 1: Three-Dimensional Structure of Molecules

Purpose

To illustrate the three dimensional shape adopted by the electron pairs surrounding the central atom in a molecule or ion.

Materials

9 Balloons, 10-in
6 File cards, 3" x 5", used to identify bonded atoms and lone electron pairs
Double-sided transparent tape to attach file cards to balloons

Procedure

1. Instruct student volunteers to blow up the balloons to the same size. Tie the balloons together into sets as follows: one set of three tied together and three sets of two tied together.
2. Display the shape of one pair of balloons. Show that they are linear. Explain to students that this arrangement is analogous to a molecule such as BeH_2.
3. Display the three balloons tied together. Note that they form a planar triangle with bond angles of 120°. This arrangement represents a molecule such as BCl_3.
4. Take 2 two-balloon sets and push them together to form a square planar arrangement. Mention to the students that this is one possible way to represent a molecule like CH_4. Point out that the balloons are 90° apart. Then push or "pop" the one set against the other so that the balloons form a three-dimensional shape. Point out that this is a tetrahedral shape and that the electrons are farther apart than in the square planar arrangement.
5. Place a 3" x 5" card on one of the balloons in the tetrahedral arrangement to represent a nonbonding electron pair. Mention that the electron pair occupies the same space as a bond, perhaps even more. Note that the resulting pyramidal structure (pretending that the balloon with the card is not seen) represents a molecule like NH_3 (three electron pair bonds, one unshared pair).
6. Place another 3" x 5" card on a second balloon to represent another nonbonding pair of electrons. Note the bent, planar shape as in H_2O, which has two bonded atoms and two unshared pairs (the balloons with the cards).
7. Display the tetrahedral arrangement once again with another card in place on a third balloon. Note that there is only one bonding site available, and that the resulting molecule is again linear. This is analogous to the bonding in HF.
8. Extend the demonstration by placing five balloons together (one set of two and the set of three). The balloon pair may be twisted around the center of the balloon trio. These five form a structure called trigonal bipyramidal, such as PCl_5.
9. Place six balloons together by twisting a balloon pair around the center of the balloon tetrahedron. An octahedral structure will form. Show the eight sides or faces that are the basis for the name. An example of an octahedral molecule is SF_6.

Remarks

This demonstration may be used either for a pre-laboratory or post-laboratory discussion for *Activity 1*, or it may be used to introduce the VSEPR concept. Ten min of teacher preparation time is needed to try the demonstration prior to performing it for students. 20-30 min are needed to perform the demonstration.

There are no particular safety hazards involved with the demonstration. Have students inflate the balloons to get them involved. Instruct them to make the balloons nearly the same size.

It is helpful to have solids in the shape of a tetrahedron, a trigonal bipyramid, and an octahedron to show the origin of names given to molecular shapes while pointing out that the orientation of electron pairs determines the overall shape of the molecule. This fact is not always obvious to students. Otherwise, little discussion is needed other than to point out what each balloon set represents.

Reference

(Based in part on: Demonstration B25 in *Doing chemistry*. (1988). Washington, DC: American Chemical Society.)

Demonstration 2: Polar Molecules

Purpose

This demonstration shows typical behaviors for a polar liquid (water) and a nonpolar liquid (hexane or kerosene).

Safety

Hexane and kerosene are toxic by ingestion or absorption through the skin. Both are highly flammable and must not be used near open flames. Safety goggles must be worn.

Materials

2 Burets, 50- or 100-mL and clamps; ringstand
2 Beakers, 400-mL or larger
Water, 100 mL
Hexane or other nonpolar liquid *(do not use toxic or carcinogenic liquids)*, 100 mL
Hard rubber or glass rod (or use plastic pen and rub with paper toweling)
Cat fur or wool or silk (cat fur or wool with rubber rod or silk with glass rod)

Procedure

Fill two burets with two liquids, water in one and a nonpolar liquid in the other. Have a rubber rod or glass rod and the material to rub it with nearby. Open the stopcock or adjust the clamp to obtain a thin, unbroken stream flowing into a beaker. Charge a rod by rubbing it with appropriate material. Bring the charged rod near the stream of liquid and have students state what is observed. If the stream is water, then the stream will be attracted to the rod and its path changed. Repeat with the other liquid.

(An alternate procedure is to use two paper cups, two bowls or beakers, and a balloon. Use water and kerosene for the liquids. First, use a small pin to put a small hole in the center of each paper cup's bottom. Then place one of the liquids in a cup and let it slowly stream into the bowl. Rub the balloon against a wool coat or sweater (or rub it against a person's hair), and then bring it close to the liquid stream. The bending of the water stream is quite obvious. Students seem to enjoy it more when it is done this way.)

Remarks

About 15 min are needed to get the materials together and try the demonstration. Onlyabout 10-15 min are required to perform the demon-stration.

The demonstration is probably best used in conjunction with the activity on molecular shapes. It could be used to pose a question that may be answered in terms of the polarity of molecules. In some respects it is counterintuitive since one does not ordinarily expect the result obtained.

There are variations to this demonstration. Its placement depends upon your preference and approach. It also fits well with a consideration of chemical bonding to illustrate polar molecules. It is included here to emphasize that molecular shape is important in determining molecular polarity.

Why is one stream attracted to the charged rod? (Bassam Z. Shakhashiri *Chemical Demonstrations: a Handbook for Teachers of Chemistry,* Volume 3. The University of Wisconsin Press, 1989, 329-332. I. D. Brindle and R. H. Tomlinson, *J. Chem. Educ.* 52:382 (1975).)

Polar molecules are themselves attracted to charges. Moreover, polar molecules support dissocation. Unless purified and stored with extreme care, polar liquids tend to form conducting solutions. The charged rod causes a net separation of charges in the bulk liquid. When droplets form at the end of the stream, they have a net charge and are attracted to the rod. (Friction of moving nonpolar liquids also causes charge separation; that is why gasoline tankers that move large amounts of liquid are grounded to receptacles as fuels are pumped. Failure to ground can lead to large static electric discharges and result in explosions.)

References

Based in part on the demonstration "Bending a Stream of Water" in Summerlin, L., Borgford, C., and Ealy, J. (1987). *Chemical demonstrations: A sourcebook for teachers, Volume 2.* Washington, DC: American Chemical Society. CHEM STUDY film (video) on "Shapes and Polarities of Molecules" has a lengthy version of this demonstration (see *Media*).

Alternate procedure suggested by Doris Kolb.

Demonstration 3: Demonstration Models

Purpose

To build a set of demonstration models that show the "ideal" geometry (shapes) for the molecular shapes taught using VSEPR theory.

Materials

15 Styrofoam® spheres, 76-mm diameter
40 Styrofoam® spheres, 50-mm diameter
8 Egg-shaped Styrofoam® figures, about 76- x 50- to 70-mm (lone pairs)
9 Feet 3/16-in diameter Dowel stick
Suitable glue for gluing Styrofoam® to wood
Suitable device for measuring and marking angles on the 2" spheres
Ice pick or carpenter's awl or some other sharp-pointed tool
Drawing compass and poster board
Styroglue® (craft or hobby store)

Procedure

Use these models when introducing students to VSEPR theory. It shows students concrete examples of a rather abstract idea. Keep in mind that the shapes constructed are idealized. Begin with the simplest case, AX_3, and explain why that shape is assumed by the molecule in terms of minimizing electrostatic repulsion between the three regions of high electron density on the central atom. Continue in this fashion until all the molecular shapes that will be used by the class have been discussed. This may extend through the tetrahedral case, or may include all the cases, depending upon the ability of the class. Please note that the trigonal bipyramid is not intuitively the shape of choice for five electron pairs on the central atom; a square pyramidal arrangement with all angles equal to 90° seems more likely to students. A somewhat sophisticated geometric argument is required to illustrate that the trigonal bipyramidal shape minimizes repulsion between electron pairs.

Remarks

Building a set of models requires a substantial investment of time; therefore, the task must be started well in advance. However, once built, the models can be used again and again. An alternative is to purchase a demonstration-sized set of snap-together molecular models. Most major science suppliers have these available, but they are expensive.

Models are useful from the consideration of molecular geometry through the remainder of the course whenever models are needed.

1. To measure and mark angles on the Styrofoam® spheres, use the technique described in *Advance Preparation* for *Activity 1*. In addition to a triangular template to mark 120° angles, one to mark 90° angles is also needed. Both templates need a circular hole to fit the 76 mm spheres. The ice pick or carpenter's awl are convenient to make holes for the dowel stick connectors.
2. Careful selection of glue is necessary since many modeling glues will dissolve polystyrene. Elmer's™ glue works well if time is not important. Hobby shops and crafts shops will probably have an appropriate glue.

3. Egg-shaped Styrofoam® objects are available in hobby and crafts stores, particularly around Easter. These work well to represent nonbonding electron pairs.
4. Although it is not necessary, painting the spheres and egg shaped objects is a nice touch. Latex and acrylic based paints work well. Painting should be done prior to making the models.
5. Solicit volunteers from classes to help with the construction of models. This speeds up the process considerably. After school, during lunch or activity periods are convenient times to do this.
6. The only hazard in building the models is that some people are allergic to glues of one sort or another.

Demonstration 4: Two-Dimensional Analogy of Molecular Geometry

Purpose

To demonstrate a magnetically driven, two-dimensional analogue of electron pair repulsion in molecules.

Materials

Package of stainless steel sewing needles, 4-5 cm long
Strong permanent magnet or electromagnetic
Pyrex™ or clear plastic cylinder, 15-20 cm diameter
Bell wire (enough plastic coated copper wire to make 6-10 coils around a glass cylinder)
6-V Dry cell battery or direct current power supply that can produce 6 V.
Approximately 1 doz. Styrofoam® discs, 5/8-in diameter, cut from beverage cups or other sources (packing material pieces may be used).
Wax

Procedure

Tell the class that they will be shown a two-dimensional analogy to molecular geometry. Then after connecting the direct current source to the wire coils, begin with one magnetized needle assembly in the water. It should stay near the center of the dish. Add additional needle assemblies, one at a time, and note the orientation about the first needle assembly. This behavior is analogous to that of atoms bonding with a central atom to produce a particular geometry.

Remarks

This demonstration makes more sense if it is presented *after* students' first introduction to VSEPR theory.

The demonstration may be performed in 15-20 min depending upon the points made to the class. Teacher preparation time is considerable. If materials are readily available, the preparation will take about one hour.

A clear Pyrex™ glass cylinder or clear plastic cylinder 15-20 cm in diameter works well for this demonstration. After waxing the inside of the dish above and below the wire turns, fill it with water to the middle of the wire coils. Magnetize about 12 needles with all points in the same direction on one pole of a strong magnet. Prepare each needle assembly by inserting the point of a needle through one of the Styrofoam® discs. Place one magnetized needle assembly in the water and attach the two ends of the wire to the current source. If the needle moves toward the outside of the dish, reverse the polarity of the wire leads. The demonstration may be performed on an overhead projector by using a shallow dish (see Figure 2 for details of the setup).

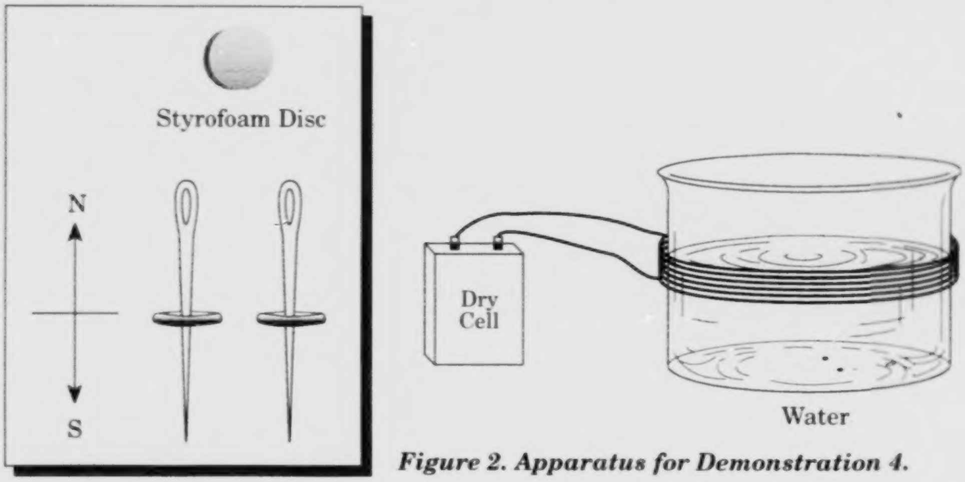


Figure 2. Apparatus for Demonstration 4.

Reference

Based on a demonstration presented by A.C. Breyer at CHEM ED 77, Beaver College, Glenside, PA 19038.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. **What are the basic assumptions of the Valence Shell Electron Pair Repulsion model of molecular structure?** *[Student answers will probably vary considerably. The answer given below is generally not published in introductory chemistry texts with the same amount of detail, and students' answers will probably give some vague idea about the first two of these. Typically, one high school chemistry textbook says that VSEPR theory states that because electron pairs repel, molecules adjust their shape so that the valence electron pairs are as far apart as possible. There are just four basic assumptions. One assumption is that all of the valence shell electron pairs of the central atom are about the same distance from the atom's nucleus. This is strictly exact for two, three, four, and six electron pairs that are bonding the central atom to a set of identical atoms or groups. The second is that electrons have the ability to rearrange themselves. The pairs arrange themselves so as to minimize repulsion. To do so they behave as if they are on the surface of a sphere behaving under an appropriate force law. This gives the most probable arrangement. The third assumption is that multiple bonds (double or triple covalent bonds) have about the same effect on molecular geometry as do single bonds. The final assumption is that nonbonding pairs occupy a larger volume of space than do bond pairs; hence they repel more strongly. Calculations based on electrostatic principles and the Pauli exclusion principle substantiate these assumptions.]*
2. **Based on VSEPR theory, what are the possible molecular shapes when representative elements form molecules?** *[See the* Appendix *for complete details in tabular form.]*

3. **Predict the molecular shapes of the following and predict whether each species is polar or nonpolar:** (a) PH_3, (b) PH_4^+, (c) SO_3^{2-}, (d) BrO_3^-, (e) CaH_2, (f) H_2S, (g) PO_4^{3-}, (h) SiF_4, (i) SO_3, (j) ClO_4^-, (k) Cl_2O, (l) N_2, (m) CCl_4, (n) NCl_3, (o) HCN, (p) PCl_5, (q) SF_6, (r) $Co(NH_3)_6^{2+}$. (HINT: First determine the number of bonds on the central atom.) *[General students should be able to answer (a) through (o), and honor students should be able to answer all of them. (a) trigonal pyramidal; polar (b) tetrahedral; nonpolar (c) trigonal pyramidal; polar (d) trigonal pyramidal; polar (e) linear; nonpolar (f) angular (bent); polar (g) tetrahedral; nonpolar (h) tetrahedral; nonpolar (i) triangular planar ; nonpolar (j) tetrahedral; nonpolar (k) bent (angular); polar (l) linear; nonpolar (m) tetrahedral; nonpolar (n) trigonal pyramidal; polar (o) linear; polar (p) trigonal bipyramidal; nonpolar (q) octahedral; nonpolar (r) octahedral; nonpolar.]*

4. **Phosphorus forms PCl_3 and PCl_5. Nitrogen forms NCl_3 but not NCl_5. Explain why NCl_5 does not exist.** *[Due to the small atomic radii of Period 2 elements (see* Periodicity *module), the maximum coordination number (CN) of any element in Period 2 is four. Thus, it is not possible for NCl_5 to exist. Furthermore, nitrogen does not have any low-lying d orbitals available to form the required bonds. Phosphorus can utilize the 3d orbitals in forming the extra bonds.]*

5. **Explain what is meant by a polar molecule.** *[A polar molecule is one in which there is an asymmetric distribution of charge. Due to both differences in electronegativity between the atoms forming bonds and the shape of the species, electron density is not evenly distributed, resulting in apparent separation of charge.]*

6. **Must a polar molecule contain a polar bond? Explain.** *[Yes. Otherwise, there will be no permanent separation of charge.]*

7. **The bond angles in NH_3, H_2O, and CH_4 are 107°, 104.5°, and 109.5°, respectively. How can these values be justified if the central atom in each has four electron pairs in its valence structure?** *[CH_4 has four bond pairs and no lone pairs, H_2O has two bond pairs and two lone pairs, NH_3 has three bond pairs and one lone pair. Lone pairs exert a greater repulsion than do bond pairs. As the number of lone pairs increases, the bond angle of the bond pairs decreases.]*

8. **Challenge question: predict the shapes and polarities of the following molecules and/or ions.** (a) BeH_2, (b) BCl_3, (c) SiH_4, (d) $Sb(OH)_6^-$, (e) CO_3^{2-}, (f) $Al(H_2O)_6^{3+}$, (g) $SbCl_5$, (h) $TeCl_4$, (i) BrF_3, (j) BrF_5, (k) NO_2^-, (l) N_2O. *[(a) linear; nonpolar, (b) triangular planar; nonpolar, (c) tetrahedral; nonpolar, (d) octahedral; nonpolar, (e) triangular planar ; nonpolar, (f) octahedral; nonpolar, (g) trigonal bipyramidal; nonpolar, (h) distorted tetrahedron (seesaw); polar, (i) T-shaped; polar, (j) square pyramidal; polar, (k) bent; polar, (l) linear; polar.]*

Counterintuitive Examples and Discrepant Events

1. Distribution of four electron pairs about a central atom leads to two possible structures, the square plane and the tetrahedron. Since the square planar structure is two-dimensional and easy to visualize, students often think that this structure is optimal for minimal repulsion. They must see models in order to understand that the tetrahedral angle exceeds 90°.

2. Predicting the geometry of five electron pairs is counterintuitive. Experiment shows that five electron pairs lead to a trigonal bipyramidal structure. Such a structure has two different angles; the trend in equivalent angles is broken. Analysis shows that for regular, isogonal polyhedra, only the tetrahedron, the octahedron, the icosahedron, the cube, and the dodecahedron are possible. The trigonal bipyramid is not. It is impossible to distribute five equivalent vertices into a convex polyhedron with five equivalent angles between its center and its vertices. The nonequivalent positions for coordination number = 5 lead to another counterintuitive example. All lone pairs are found in the equatorial positions (120° separation) rather than the axial positions (180° separation; see *Appendix*).

3. A third counterintuitive example is the fact that distribution of six electron pairs around a central atom can lead to a square planar molecular shape. A good example is XeF_4 (see *Appendix*).

Analogies and Metaphors

What's in a name?

1. The word "polar" is associated with ice caps, bears and regions of the earth. Few people, except chemists, think in terms of polar molecules.

2. What if polar molecules did not exist? How would our lives be affected if water were not a polar molecule? Consider the hydrogen compounds of some Period 2 elements: BH_3, CH_4, NH_3, OH_2 and FH. Of these five compounds, OH_2 is the only liquid at room temperature. OH_2 also has the highest boiling point, highest heat capacity and the lowest density in the solid state. All of these unusual properties are due to the polar nature of OH_2; if OH_2 behaved like its periodic analogs, carried to its ultimate conclusion, life as we know it would not exist [see Speakman, J. C. (1966). *Molecules*].

Pictures in the Mind

1. Molecular models are visual aids commonly used by chemistry teachers. To provide students with a hands-on activity that enhances their visualization of the three-dimensional arrangement of bond angles in common molecules, the following activity is recommended.

   To illustrate the spatial distribution of electron pairs achieving maximum spatial separation, use a piece of Play-Doh™ or modeling clay and four toothpicks per student. After materials have been distributed, instruct students to place two toothpicks in the Play-Doh™ so that they are separated as far apart as possible. The students will quickly realize that toothpicks placed at a 180° angle produce this result. Have them repeat with three and then four toothpicks. It is *not* recommended that this activity be extended to the trigonal bipyramidal structure since it is a counterintuitive arrangement (see *Counterintuitive Examples* and *Discrepant Events*). The activity might work with six toothpicks to produce an octahedral arrangement. (This idea was suggested by K. Elsen, Mount Mary College, Milwaukee, WI.)

2. Constructing models of polyhedra constitutes an excellent group activity or homework exercise. Templates can be reproduced and assembled with minimal materials: Old manila folders, scissors, glue, and transparent tape. The activities that follow work well if done as part of the pre-laboratory exercise.

Tetrahedron. Using a drawing compass, draw a circle with a 10-cm radius close to the edge of an 8 1/2 x 11" piece of heavy paper. Maintaining the same radius, place the compass point at Point A (Figure 3), and draw an arc that intersects the circle at Point B. Place the compass point on Point B and repeat to intersect the circle at Point C; repeat the procedure for Point D. Connect Points A, B, C and D with the center of the circle (E) as shown in Figure 4a. Then extend the lines A-B and D-C as shown in Figure 4b, and add tabs for gluing.

Cut around the outer edges, score the inner lines with the back of a scissors blade, fold along the lines, and glue together with a clear liquid glue.

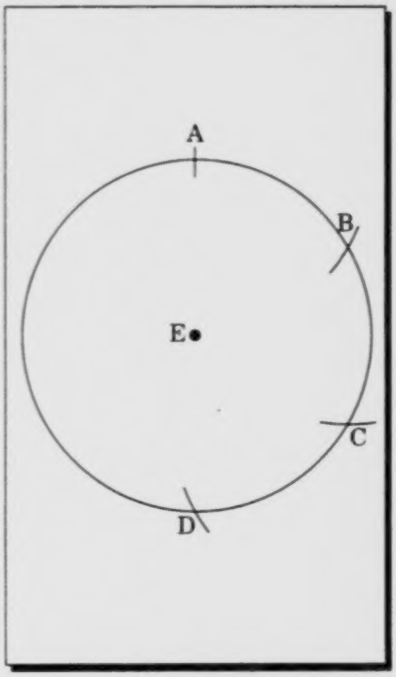


Figure 3. Arcing a circle.

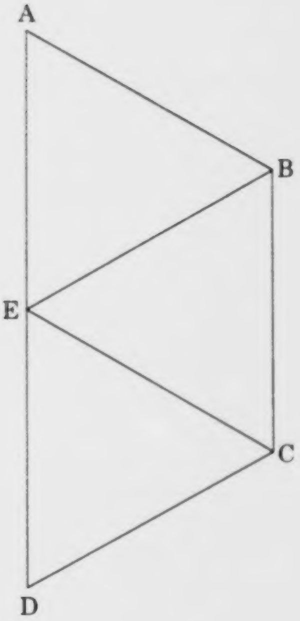


Figure 4a. Connecting points with center of circle.

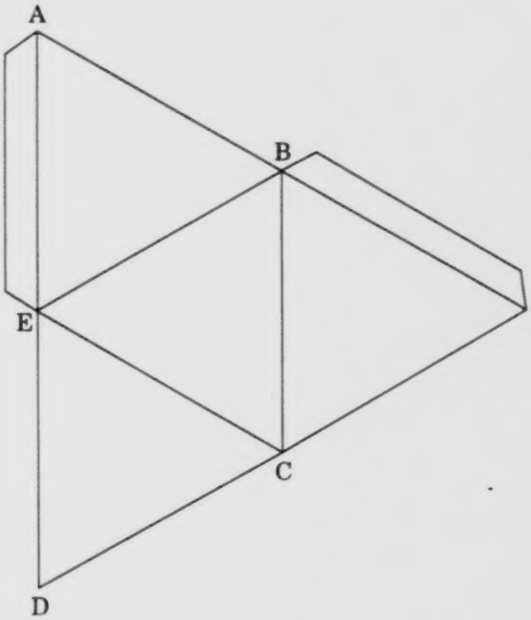


Figure 4b. Adding tabs.

Octahedron. To form an octahedron, reproduce the template provided in the *Appendix* and assemble it. Alternatively, use the same method as for the tetrahedron, but lay off *four* radii around the circle. Connect the radii as shown in Figure 5.

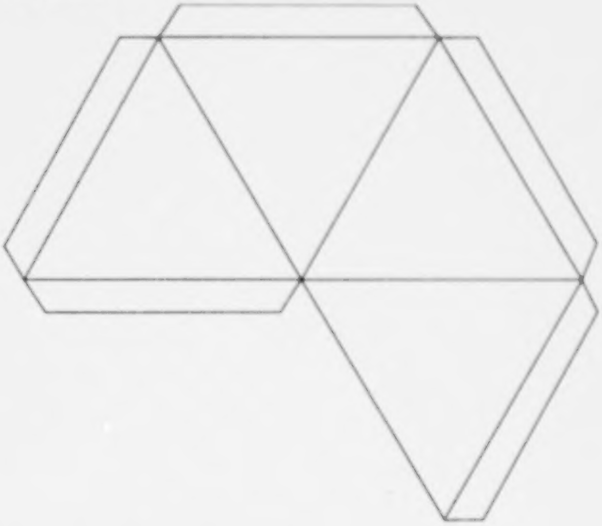


Figure 5. Connecting radii.

Make a second half like the first half. After being certain that the tabs are folded flat, glue the two halves together, putting the two square based pyramids base to base.

Trigonal Bipyramid. To form a trigonal bipyramidal structure, glue two tetrahedra base to base.

3. Polar covalent bonding in a linear molecule. Which of these sketches can be compared to a polar covalent bond?

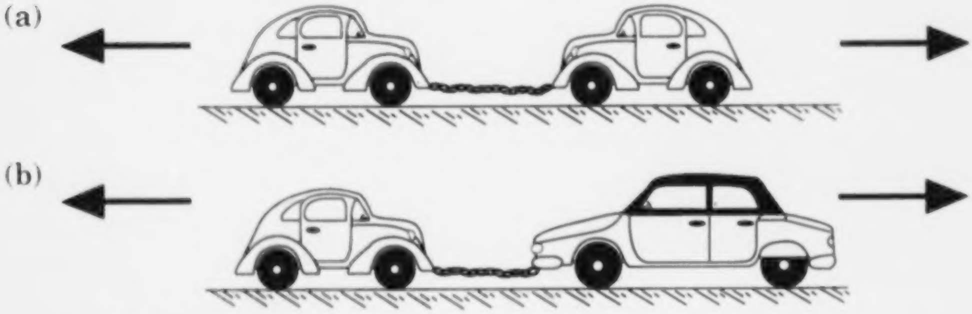


Figure 6. Polarity analogy.

TIPS FOR THE TEACHER

Language of Chemistry

The following is a minimal glossary of terms for molecular geometry:

bond pair bonding electron pair on the central atom (frequently referred to as X in generic formulas).

coordination number number of neighboring groups in contact with a central atom.

electronic geometry arrangement of bonding and nonbonding electron pairs around a central atom.

lone pair nonbonding electron pair on the central atom (frequently represented as E in generic formulas).

molecular geometry shape of a molecule resulting from covalent bonding of ligands around a central atom. Molecular geometry is not synonomous with electronic geometry (see *Common Misconceptions* for a detailed discussion).

polygon plane form made up of a number of straight sides.

polyhedron solid formed by a number of polygonal faces.

polytope general term for a solid figure like a polyhedron.

stereochemistry study of the geometric arrangement of atoms or groups of atoms around the central atom(s) in a molecule or polyatomic ion.

steric number number of bond pairs and lone pairs of electrons surrounding the central atom in a molecule.

Pattern Recognition

Refer to *Answers to Implications and Applications* for *Activity 1* for some fairly simple rules of thumb (ROTs) to help students predict both molecular geometry and molecular polarity.

Common Student Misconceptions

"The number of electron pairs surrounding a central atom is equivalent to the molecular geometry of the resultant molecule."

The word geometry has *two* different meanings when applied to molecules.

- Electronic geometry and molecular geometry have different meanings!
- Molecular geometry and shape of a molecule are the same thing.

The central organizing principle that is responsible for molecular geometry is the *number of valence pairs of electrons* that surround a central atom. That number determines the *electronic* geometry. The valence electrons distribute around a central atom in order to minimize mutual repulsion. Location of these electron pairs results in spontaneous placement at the vertices of two-dimensional polygons (*e.g.*, triangle or square) and three-dimensional polyhedra (*e.g.*, tetrahedron and octahedron).

It is first necessary to assess the number of bonds present around a central atom. The "demand/supply rule" provides a rapid answer (see *Chemical Bonding* module). A linkage is a connection between two atoms. A linkage may be a single, double, or a triple bond. When the number of linkages equals the number of valence electron pairs around the central atom, the situation is simple (an example is CH_4). The number of linkages plus the number of lone pairs is called the steric number of the central atom. The steric number always determines the electronic geometry. If the steric number is the *same* as the number of linkages, then the molecular and electronic geometries are the same. If the number of linkages is less than the steric number, it is the steric number that determines the shape of the molecule. Some examples are the following. CH_4 has four linkages (C—H connections) and a steric number of four, so the central C atom is at the center of a tetrahedron, four H atoms are the vertices, and both the electronic and the molecular geometry are tetrahedral. H_2O has two linkages (H—O connections) and two lone pairs, so the steric number is four, the *electronic geometry* is tetrahedral, and the *molecular geometry* is called bent. The steric number is also four in NH_3 so the central N atom is also at the center of a tetrahedron. The electronic geometry is tetrahedral; the molecular geometry is trigonal pyramidal (the three linkages define a triangular plane below (or above) the central N atom). SO_2 has two linkages (two S—O connections, one is a single bond, one is double bond), and one lone pair, so the steric number is three. In this case the S atom is at the center of a triangle, the two O atoms are at two of the vertices and the lone pair is at the position of the third vertex. The electronic geometry is triangular, but the molecular geometry (shape) is angular, or bent.

Problem Solving

HOT TIP: Use the "ultrafast method" to determine the electronic geometry (without taking the time to determine the Lewis structure first)!

Although this method is *based* on our knowledge of Lewis structures it is a quick trick to find electronic geometry and then molecular geometry. The advantage of the method is that you do not have to determine the Lewis structure first, saving considerable time. The method is very easy to apply to molecules containing a single central representative element (the Li, Be, B, C, N, O, F, and Ne families; H and He normally are not "central atoms"). It is best for beginners to restrict their practice to these families of molecules. They are, by far, the most common. There are only three "rules."

1. First, count the number of valence electrons for the *central atom* of the family. If the central atom is C, count "4."
2. Next, look at the atoms that are bonded to the central atom, and count the following for each of these: H, F, Cl, Br, I—1; O, S—0. (It is rare that atoms bonded to a central atom are not in this list.)
3. Add the number of electrons for the central atom and for *each* of the bonded atoms, add or subtract the charge on the species if it is not a neutral molecule, then divide the total number of electrons by two to obtain the number of repelling pairs of electrons. Remember, two pairs gives linear electronic geometry, three pairs are triangular, four pairs are tetrahedral, five pairs are triangular bipyramidal, six pairs are octahedral.

Examples:

1. **Water, H_2O**

   O is the central atom, so count 6 electrons and count 1 for each H atom, giving

   $$\frac{[6 + 2(1)]}{2} = 4 \text{ pairs—the tetrahedral geometry.}$$

   O is at the center of the tetrahedron, and the two H atoms are at two of the four vertices. The other two vertices are occupied by lone pairs. The electronic geometry is tetrahedral; the molecular geometry is bent

2. **Sulfate ion, SO_4^{2-}**

   S is the central atom, count 6 for it, 4 O atoms are bonded to it, count 0 for each of these, and the ion has a charge of 2–, so

$$\frac{[6 + 4(0) + 2]}{2} = 4 \text{ pairs}$$

Thus, the ion is tetrahedral (four pairs) with the S atom at the center, and four O atoms at the vertices.

3. **Xenon tetrafluoride, XeF_4**

Xe is the central atom, count 8 for it, each of the four bonded fluorines counts 1 each, so

$$\frac{[8 + 4(1)]}{2} = 6 \text{ pairs.}$$

The electronic geometry is octahedral 6 pairs. The four F atoms are at the vertices of a square, so the molecular geometry is square planar.

HISTORY: ON THE HUMAN SIDE

As early as 1852, E. Frankland proposed the idea of valence. A. Kekulé, in 1858, and A. W. H. Kolbe, in 1859, extended this concept by proposing the quadrivalency of the carbon atom; Kekulé then suggested that carbon atoms could bond to one another in indefinite numbers to form a chain. A. S. Couper, in the same year, introduced the concept of a valence bond and drew the first structural formulas.

A. M. Butlerov, in 1861, introduced the term chemical structure and stressed the importance of writing a single formula for a compound showing how the atoms were linked together in one of its molecules.

The tetrahedral structure of the carbon atom was independently recognized two months apart in 1874 by J. H. van't Hoff and J. A. Le Bel. A. Werner worked on deducing the stereochemistry of complex compounds from 1893 to 1905. In 1916, G. N. Lewis introduced his theory of valence, which was followed by a period of development leading to the quantum mechanical valence bond and molecular orbital theories. Linus Pauling is frequently called the father of modern structural chemistry. During the time period 1930-1933, he published seven papers applying quantum mechanics to chemical bonding that elucidated the nature of the chemical bond. Pauling received the 1954 Nobel Prize in chemistry for this work.

In 1962, Neil Bartlett synthesized a xenon compound, the first recorded instance of the preparation of a noble gas compound. The study of noble gas compounds has contributed greatly to our understanding of chemical bonding and molecular structure.

Dorothy Crowfoot Hodgkin spent most of her career teaching and doing research using X-ray crystallographic analysis. This method led to the structure determination of a number of complex molecules from natural sources including penicillin, vitamin B_{12}, and insulin. Hodgkin was awarded the 1964 Nobel Prize in chemistry for this work.

W. N. Lipscomb, Jr. during the period of time, 1952-1976, did pioneering research on the structure of the boron hydrides that led to a better understanding of molecular structure and chemical bonding. For this work, he received the Nobel Prize in 1976.

Isabella L. Karle developed an analytical technique to use with X-ray diffraction that has made important contributions in the field of X-ray crystallography. This work enabled her husband, Jerome Karle, to gain acceptance for his work on key mathematical techniques through which X-ray crystallography can be used directly to determine the three-dimensional structure of natural substances.

HUMOR: ON THE FUN SIDE

1. Ball-and-stick models are frequently referred to as "chemical tinker toys."
2. When using Styrofoam® spheres for models, welcome students to the "ball room."
3. A cup of coffee is the model for $Co(Fe)_2$.
4. Word Search (see *Appendix* for master copy)

P P A O V Y Z V Y ~~R I A P E N O~~ L
~~M O L E C U L A R G E O M E T R Y~~
O X L D J R Y A F C T N J F P Y S
V N J Y T Z I T P T V L Q U Q H C
J I J F G P W V M Z A M H I V C V
R Y L O K O E Y M P L V J Q O U Z
I R B I I L ~~N O R D E H Y L O P~~ G
A T E X R Y J J E R N F E D J Q R
P T G S Y T L J A C C N J G S M C
D F D X V O C B K V E T X V F Q E
N R W K G P U A P T Z V O Z C E S
O C J ~~S T E R I C N U M B E R~~ D W
B ~~S T E R E O C H E M I S T R Y~~ R

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Bonding electron group contributing to entry 8 (two words).
2. Nonbonding contributor to entry 8 (two words).
3. Shape of a molecule (two words).
4. Plane form made up of a number of straight sides.
5. Solid formed by a number of polygonal faces.
6. General term for a solid figure like a polyhedron.
7. Geometric arrangement of atoms or groups around the central atom in a molecule.
8. Number of bond pairs and lone pairs of electrons surrounding the central atom in a molecule (two words).
9. Combining ability of an atom based upon the number of electrons in its outer shell.
10. Acronym for theory to describe the forces resulting in the geometry of a molecular species.

Answers: 1. BOND PAIR 2. LONE PAIR 3. MOLECULAR GEOMETRY 4. POLYGON 5. POLYHEDRON 6. POLYTOPE 7. STEREOCHEMISTRY 8. STERIC NUMBER 9. VALENCE 10. VSEPR

5. See cartoons at end of module.

MEDIA

Many computer programs that use graphics to show molecular structure are available. Prices vary, and programs can be found for almost any microcomputer.

1. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
    a. *Bravais*, by Philip Pavlik. Vol. III B, No. 1, for IBM PS/2 PC-compatible computers.
    b. *Alkane Isomers*, by Richard R. Hiatt. Vol. VI V, No. 1, for IBM PS/2 PC-compatible computers.
    c. *MolVib*: Visualizing Molecular Vibrations, by Daniel Huber. Vol. III C, No. 1, for the Apple Macintosh.
    d. *Proton NMR Spectrum Simulator*, by Kersey Black. Vol. II C, No. 1, for the Apple Macintosh.
    e. *Evolution of Bonding Theory*, by David Whisnant. Vol. II A, No. 1, for the Apple II computer.
    f. *Crystal Lattice*, by David Trapp. Vol. IV A, No. 1, for the Apple IIGS computer.
2. Software published by Falcon Software, Box 200, Wentworth, NH 03282; (603) 764-5788.
    a. *Lewis Structures and Molecular Geometry*, by Jeffrey R. Buell, Andrew F. Montana and Patrick A. Wegner. For the Apple Macintosh. $95 for individual copies.
    b. *Molecular Editor*, by Allan Smith. For the Apple Macintosh. $50 for individual copies.
    c. *Valence Shell Electron Pair Repulsion Theory*, by Michael P. Doherty. For IBM computers. $50 for individual copies.
    d. *SpectraBook* for Windows and *SpectraDeck* for Macintosh – An Annotated Collection of IR, NMR, CMR and Mass Spectra, by Paul F. Schatz. $95 for individual copies.
    e. *The Schatz Index* for Macintosh, by Paul F. Schatz. The IR and NMR spectra, physical information, references, synonyms and safety data for 400 organic compounds. $200 for individual copies.
    f. IR and NMR Simulators of Macintosh and MS-DOS. These simulators are low-cost and easy to use; they are no-maintenance simulations of the real instruments. Data sets for 300 compounds are available separately. $95 for individual copies of NMR simulator, $75 for individual copies of IR simulator, $200 for IR data set, $250 for NMR data set.
3. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).
    a. For the Apple II computer running on ProDOS: AR 303.
    b. For the Apple II computer: AP 301, AP 310, AP 704, AP 705, AP 706.
    c. For IBM PCs and PC-compatibles: PC 2801, PC 2802, PC 2803, PC 3501.

4. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   "Carbon and Its Bonds," "Chiral Molecules and Polarized Light," "From an Amino Acid to a Peptide Chain," "The Alpha Helix," "Hair and Silk, "The Boat and Dock Model, and "DNA Structure, Synthesis of Messenger RNA, Protein Synthesis," seven chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc II (double sided, 60 min.), Special Issue 4.

5. *MacMolecule,* V. 1.7, by Eugene Meyers, Carlos Blanco, Richard B. Hallick and Jerome Jahnke, Department of Computer Science, University of Arizona, Tucson, AZ 85721. Interactive 3D molecular modeling curriculum development shareware program featuring a video animation generation program and a molecular image database. For Apple Macintosh computer with math coprocessor.

6. Materials and devices from ICE–Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-3033 (voice) or (608) 262-0381 (FAX).

   a. The Solid State Model Kit.

   b. The Optical Transform Kit.

7. CHEM Study films/videos available from Ward's Natural Science Establishment, Inc., 5100 West Henrietta Road, P.O. Box 92912, Rochester, NY 14692-9012; (800) 2660.

   a. *Shapes and Polarities of Molecules.* This video develops the relationship between polarity and structure from an experimental point of view. The molecular dipole model is extended to explain differences in solubility, conductivity and chemical reactivity.

   b. *Molecular Spectroscopy.* Laboratory experiments, molecular models and animation show the infrared light absorption process and its relation to molecular properties. The video stresses the concept of natural molecular vibrational frequencies and inclues the method of using infrared spectroscopy to identify molecules and determine their structure.

8. *Ball and Stick* for the Macintosh computer is available on some bulletin boards and from Educorp Computer Services, 7434 Trade Street, San Diego, CA 92121-2410; (800) 843-9497; (619) 359-2502.

9. *VSEPR* (for the Macintosh; requires HyperCard) is available from John Gelder, Department of Chemistry, Oklahoma State University, Stillwater, OK 74078; (800) 633-1176.

10. *Molecular Editor,* for the Macintosh is available from Jan Biros, Microcomputing Department, Drexel University, Philadelphia, PA 19104. This is a software-based molecular model kit.

11. *Modeler: Molecular Design Editor* and *Molecular Animator* are two programs available from Sargent Welch, P.O. Box 1026, Skokie, IL 60076-1026; (800) 677-0624. Written for both Apple II and IBM-PC computers, they allow viewing ball-and-stick molecular models from different angles by rotation. Each program is approx. $100.

EQUIPMENT

Ball-and-stick models and Styrofoam® spheres of various sizes are available from most major scientific supply houses. For example, Sargent-Welch, Cenco, Science Kit, Ward's, Flinn Scientific and Fisher Scientific all have a variety of kits available at reasonable prices. Flinn Scientific has an inexpensive Styrofoam® sphere kit with a tetrahedral template included. Another source is your local hobby shop.

There are several molecular model kits that are relatively inexpensive and designed for use by large student groups. For example, one kit contains twelve packets that allows students to construct models with linear to tetrahedral centers. Most inexpensive kits are variants of ball-and-stick models. Orbit® and Minit® model systems are also available either in individual student kits or class kits that may be made up into individual packets using zip-closure plastic bags. Supplier: Aldrich Chemical Company, Inc., 1001 West Street Paul Avenue, Milwaukee, WI 53233, 1-800-558-9160.

Links/Connections

WITHIN CHEMISTRY

Molecular geometry can be linked to physical properties and chemical properties of substances. Pertinent modules are *Chemical Bonding, Organic Chemistry, Chemistry in Medicine, Polymers,* and *Enzymes.*

1. When retinal, a compound located in the retina of the eye, absorbs photons of visible light, its molecules change from the *cis* form to the *trans* form. This change in molecular geometry causes a signal to be transmitted from the retina along the optic nerve to the brain.
2. In diamonds, silicates, and carborundum (SiC), the atoms are arrayed in tetrahedral geometry, whereas in graphite, the carbon atoms have a trigonal planar arrangement.
3. In organic chemistry, sulfur tetrafluoride (SF_4) and xenon oxytetrafluoride ($XeOF_4$) are used as fluorinating agents. SF_4 has a see-saw (irregular tetrahedral) shape, whereas the xenon compound has a square pyramidal shape. What might you expect the geometry of SOF_4 to be? *(Trigonal bipyramid)*
4. To determine the molecular geometry of a molecule, one must ascertain the location of the constituent atoms. Diffraction methods involve the formation of diffraction-interference patterns that result from the scattering of X-rays (X-ray diffraction), electrons (electron diffraction), or neutrons (neutron diffraction). Spectroscopic methods that include microwave, Raman, and infrared spectroscopy rely upon energy transfer interactions between electromagnetic radiation and matter.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

Shapes of many molecules have been directly linked to their function in biological systems. Molecular geometry concepts and techniques are highly applicable in molecular biology, pharmacology, genetic engineering, medicine, *etc.*

TO THE CONTEMPORARY WORLD

1. **Drugs.** The physiological activity of many prescription and OTC drugs is due to the shape of specific functional groups in the molecule (see *Chemistry in Medicine* module).
2. **Crystal Structure.** The shape of an individual molecule dictates the crystal structure of its aggregates.
3. **Biochemistry**. Enzymes owe their activity to active sites that interact with substrates with the correct geometry. Since enzymes are crucial to the functioning of all living things, there is a direct, personal link between molecular geometry and life. Furthermore, the conformations of proteins, nucleic acids, and other substances making up the human body determine its macroscopic structure.
4. **Societal**. Synthetic polymers are extremely important substances to a highly developed technological society. The desirable properties of polymers depend on molecular conformation, but because of these same properties, polymers are also disposal problems and environmental pollutants.

Extensions

1. Research methods to measure the polarity of some covalent molecules.
2. What contributions did Jacobus van't Hoff make to understanding three-dimensional structures of molecules?
3. Make models of a family of compounds such as H_2O, H_2S, H_2Se, and H_2Te and relate bond angles to the predictions of VSEPR theory.
4. How did Linus Pauling use quantum mechanical theory to describe chemical bonds?
5. There are some compounds in which one atom has more electrons than the corresponding noble gas. PCl_5, SF_6, and IF_7 are examples. Write electron configurations for the central atoms in each one, and draw Lewis-dot structures for the compounds. Using the valence configuration of the central atoms, develop a VSEPR procedure to describe these molecules.
6. Using appropriate sized spheres and connectors, construct a model set including the following: AX, AX_2, AX_3, AX_2E, AX_4, AX_3E, AX_2E_2, AX_5, AX_4E, AX_3E_2, AX_2E_3, AX_6, AX_5E, and AX_4E_2.

References

Module developed by Royace Aikin, Daniel Kallus, and Russell D. Larsen, the Texas team.

Brey, W. (1965). *Physical methods for determing molecular geometry.* New York, NY: Reinhold.

An excellent summary of the many instrumental methods used to determine molecular geometry.

Brooks, D. W. (Producer). (1989). *Doing chemistry.* [Videodiscs, computer program, and supporting materials]. Washington, DC: American Chemical Society.

This is an excellent teacher resource. It provides hard copy of all the experiments and demonstrations; it also provides a planning toolkit, all of the experiments and demonstrations on videodisc, a computer program to interface the videodiscs with a Macintosh computer, and other useful information on computer disc. It is quite interesting and informative to watch a chemical reaction such as a dust explosion one frame at a time, which is possible with this resource.

Day, Jr., Clyde, M., and Selbin, J. (1962). *Theoretical inorganic chemistry*. New York, NY: Reinhold.

Although some of the material in this textbook is dated, it still is a valuable resource for chemical bonding and molecular structure.

McQuarrie, D. A., and Rock, P. A. (1984). *General chemistry.* New York, NY: W. H. Freeman and Company.

This book is an excellent general chemistry reference for the teacher. It contains extensive coverage of the same topics taught in a typical high school chemistry course, but in greater depth.

Parry, R. W., Bassow, H., and Merrill, P. (1987). *Chemistry: Experimental foundations.* Englewood Cliffs, NJ: Prentice-Hall, Inc.

The only CHEMS derived text currently published. Very good information, especially how to present chemistry from an experimental point of view. The companion teacher's guide is a must.

Ryschkewitsch, G. E. (1963). *Chemical bonding and the geometry of molecules.* New York, NY: Reinhold.

A plausible exposition of modern thoughts in structural chemistry.

Speakman, J. C. (1966). *Molecules.* New York, NY: McGraw-Hill.

Summerlin, L. R., Borgford, C. L., and Ealy, J. B. (1987). *Chemical demonstrations: A sourcebook for teachers, (2).* Washington, DC: American Chemical Society.

Many of the demonstrations are highly useful in an introductory chemistry course. This should be a part of every chemistry teacher's library.

Toon, E. R., and Ellis, G. L. (1973). *Foundations of chemistry (2nd Ed.).* New York, NY: Holt.

This high school chemistry textbook is loaded with valuable information about all aspects of general chemistry. It provides more historical data than most current high school textbooks and has nice vignettes about outstanding scientists. Another useful feature is the inclusion of special sections, *e.g.*, chromatography.

Wilbraham, A. C., Staley, D. D., Simpson, C. J., and Matta, M. S. (1987). *Addison-Wesley chemistry* (Teacher's Edition). Menlo Park, CA: Addison-Wesley.

A good, solid high school chemistry textbook that may be used by both novice and experienced teachers. Other equally good textbooks are available.

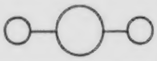
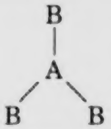
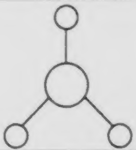
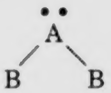
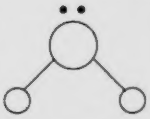
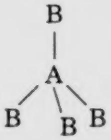
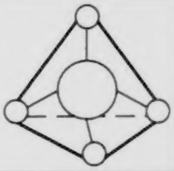
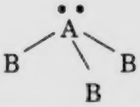
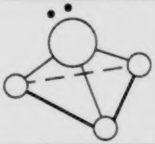
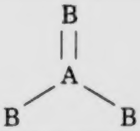
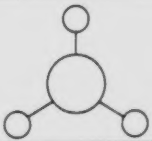
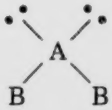
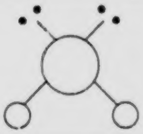
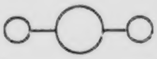
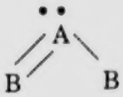
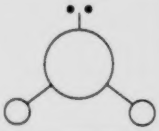
Zumdahl, S. S. (1986). *Chemistry*. Lexington, MA: Heath.

A well written and understandable freshman chemistry textbook. It can serve as an invaluable resource for the teacher.

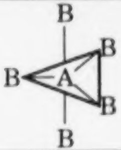
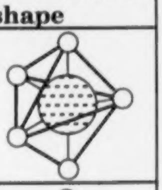
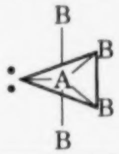
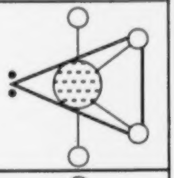
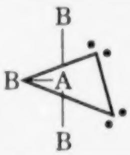
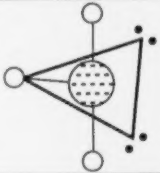
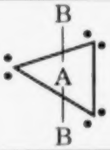
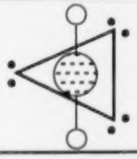
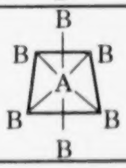
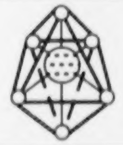
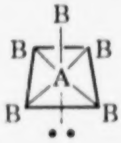
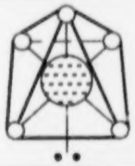
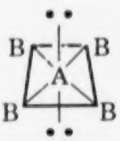
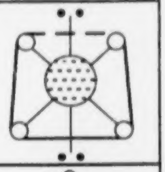
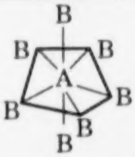
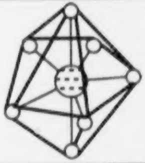
Appendix

- **Transparency Masters**
    1. Molecular Shapes of Species Containing Representative Elements
    2. Molecular Shapes of Species Containing 5, 6, or 7 Electron Pairs
    3. Octahedron Template
    4. Word Search
- **Humor**

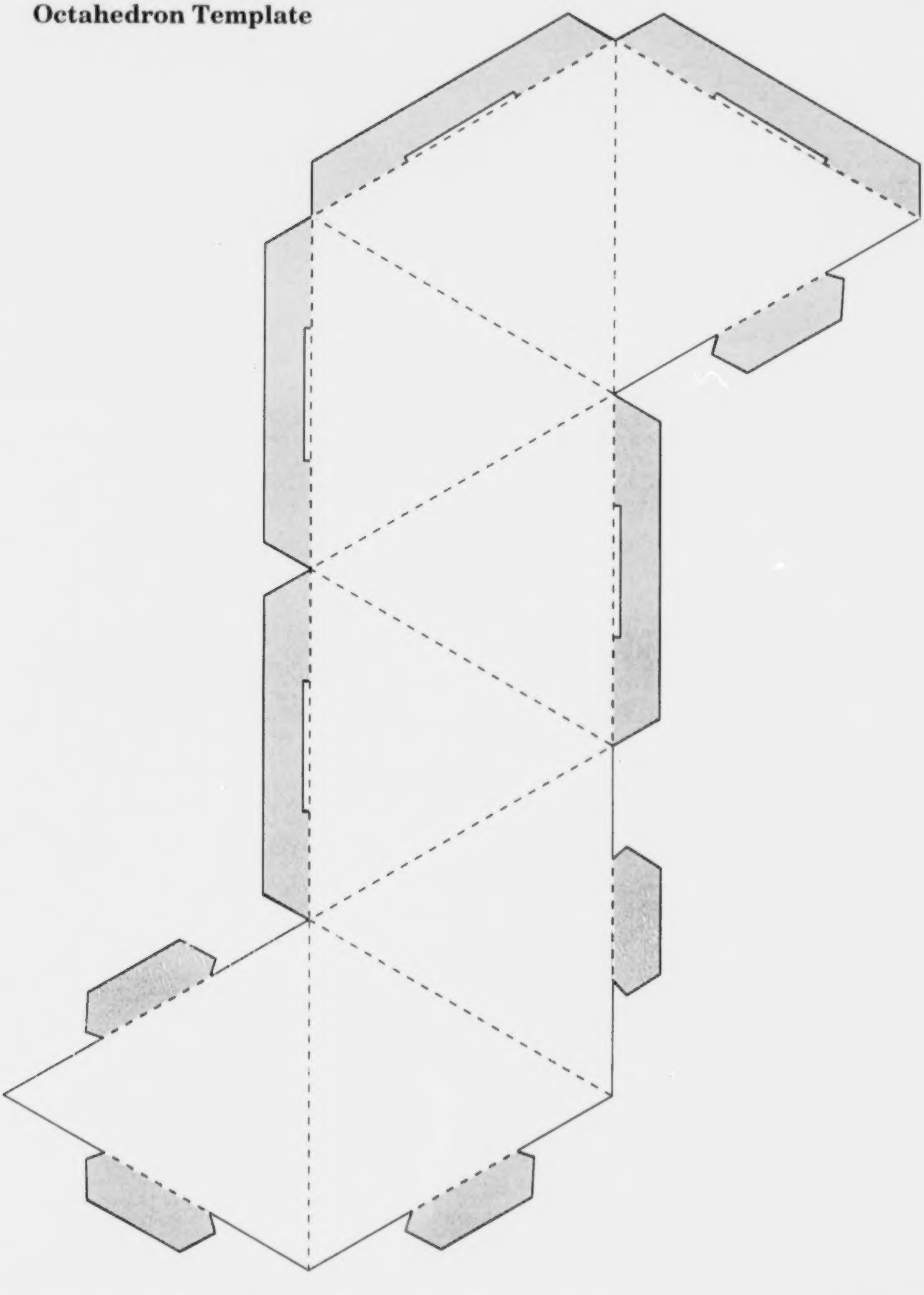
Molecular Shapes of Species Containing Representative Elements

Name of shape	Formula	No. of unbonded electron pairs (lone pairs)	No. of electron pairs in valence level of central atom	Lewis structure	Representation of shape
Linear	AB_2	Zero	2	B—A—B	BeF_2 
Trigonal planar	AB_3	Zero	3		BF_3 
Angular	AB_2	One	3		$SnCl_2$ 
Tetrahedral	AB_4	Zero	4		CCl_4 
Pyramidal	AB_3	One	4		NH_3 
Trigonal planar	AB_3	Zero	4		SO_3 
Angular	AB_2	Two	4		H_2O 
Linear	AB_2	Zero	4	B=A=B	CO_2 
Angular	AB_2	One	4		SO_2 

Molecular Shapes of Species Containing 5, 6, or 7 Electron Pairs

Name of shape	Formula	No. of unbonded electron pairs (lone pairs)	No. of electron pairs in valence level of central atom	Lewis structure	Representation of shape
Trigonal bipyramidal	AB_5	Zero	5		PCl_5 
Seesaw	AB_4	One	5		SF_4 
T-shaped	AB_3	Two	5		ClF_3 
Linear	AB_2	Three	5		XeF_2 
Octahedral	AB_6	Zero	6		SF_6 
Square-based pyramidal	AB_5	One	6		IF_5 
Square planar	AB_4	Two	6		XeF_4 
Pentagonal bipyramidal	AB_7	Zero	7		IF_7 

Octahedron Template



Word Search

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P P A O V Y Z V Y R I A P E N O L
M O L E C U L A R G E O M E T R Y
O X L D J R Y A F C T N J F P Y S
V N J Y T Z I T P T V L Q U Q H C
J I J F G P W V M Z A M H I V C V
R Y L O K O E Y M P L V J Q O U Z
I P B I I L N O R D E H Y L O P G
A T E X R Y J J E R N F E D J Q R
P T G S Y T L J A C C N J G S M C
D F D X V O C B K V E T X V F Q E
N R W K G P U A P T Z V O Z C E S
O C J S T E R I C N U M B E R D W
B S T E R E O C H E M I S T R Y R
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Bonding electron group contributing to entry 8 (two words).
2. Nonbonding contributor to entry 8 (two words).
3. Shape of a molecule (two words).
4. Plane form made up of a number of straight sides.
5. Solid formed by a number of polygonal faces.
6. General term for a solid figure like a polyhedron.
7. Geometric arrangement of atoms or groups around the central atom in a molecule.
8. Number of bond pairs and lone pairs of electrons surrounding the central atom in a molecule (two words).
9. Combining ability of an atom based upon the number of electrons in its outer shell.
10. Acronym for theory to describe the forces resulting in the geometry of a molecular species.

ALL THUMBS CHEMICAL CO.

"Sorry George . . . looks too expensive for us."

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WELL, YES, I GUESS YOU COULD CALL IT A FORM OF HARD WATER BUT— —OH, FORGET IT.

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A SourceBook Module

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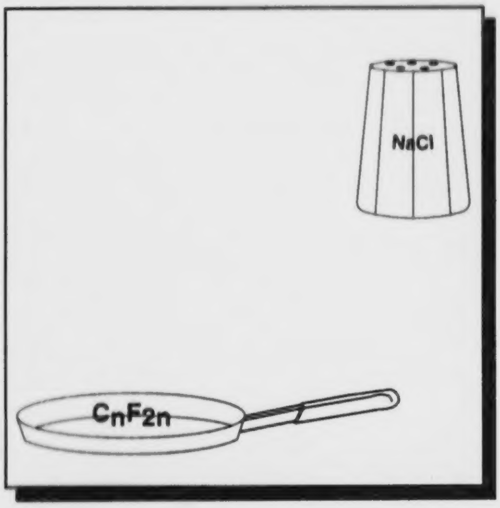
HALOGENS



ChemSource

Instructional Resources for Preservice and Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

The elements fluorine, chlorine, bromine, iodine, and astatine form a group or family in the Periodic Table known as the *halogens* (salt formers). As a group, these elements are unique in several ways. All three states of matter are represented by halogens at room temperature and one atmosphere pressure: fluorine and chlorine are gases, bromine is a liquid, and iodine and astatine are solids. As elements, all exist as diatomic molecules. Because of their high reactivity, halogens are not found free in nature, but are usually produced from halide salts.

When considering the halogens, particularly during laboratory activities and demonstrations, one usually concentrates on chlorine, bromine, and iodine. There is a good reason for this. All known isotopes of naturally occurring astatine are radioactive with relatively short half-lives. It is estimated that only a few milligrams of astatine exist at the earth's surface at any particular time. Fluorine, on the other hand, has a single stable isotope and is the second most abundant of the halogens at the earth's surface—if the hydrosphere and lithosphere are combined; chlorine is most abundant. But fluorine is the most reactive of all elements, reacting with all other elements except the noble gases helium, neon, and argon. Fluorine, which is prepared by electrolysis, cannot be used for reactions in water solution because it oxidizes water, but can be stored in stainless steel vessels because protective fluoride coatings are formed.

The most obvious chemical property of halogen elements is their ability to act as oxidizing agents. The relative oxidizing ability of halogens corresponds to their order in the Periodic Table, $F_2 > Cl_2 > Br_2 > I_2$. This trend can be amply shown by a student laboratory activity and/or teacher demonstration and correlated to trends in atomic size, electron affinity, and electronegativity. Commercially, Cl_2 is obtained by the electrolysis of NaCl solution; Br_2 and I_2 are, in turn, produced by Cl_2 oxidation of Br^- and I^-, respectively. For example:

$$Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$$

A major use of Cl_2 is in water treatment, where its action on pathogens has led to enormous improvement in the public's general health. All halogens are extensively used in the synthesis of organic compounds where properties may be tailored by replacing hydrogen atoms with halogen atoms. Of particular note are Freons and halogen-containing polymers such as polyvinyl chloride (PVC) and fluorine-containing Teflons. Many of these halogenated hydrocarbons have been found to be highly toxic, potential carcinogens or, as in the case of Freons, environmentally unsound and so have been or are being removed from general use.

All halogens, with the exception of fluorine, exhibit oxidation states of −1, 0, +1, +3, +5, and +7 (F exhibits only −1 and 0). The most common state is the halide or −1 state; crystalline metallic halides are common compounds. The iodide ion is a reasonably good reducing agent and can cause the reduction of metallic ions such as Fe^{3+} to Fe^{2+} and Cu^{2+} to Cu^+. A clear distinction must be made between elemental halogens and halide ions during the study of "halogens."

Oxoanions and oxyacids of halogens are themselves potent oxidizing agents that, in the form of "bleaches," "cleaners," or pool additives, find their way into consumer products. Common liquid "chlorine" bleaches are not chlorine water solutions, but rather sodium or calcium hypochlorite solutions; the hypochlorite ion does the bleaching. *It should be emphasized that chlorine bleaches and ammonia-containing cleansers should never be mixed, since they react to form very toxic chloramine (NH_2Cl).*

The importance of halogens to human history is detailed later, as are links between halogen chemistry and issues of importance to our everyday lives.

PLACE IN THE CURRICULUM

This descriptive module can be used in the first-year chemistry in a variety of places, either as a free-standing module taking cognizance of the related concepts and skills noted below, or selected parts of the module can be used in two or more parts of course(s) in multi-year chemistry/science curricula. For example, much of the material can be integrated into study of oxidation-reduction. Also, chemical and physical properties of halogens can be used as a part of a unit of study on the Periodic Table.

CENTRAL CONCEPTS

1. Halogens comprise a highly reactive family of elements that do not exist in the free state in nature but can be prepared electrochemically or chemically from halide melts or halide solutions (see *Laboratory Activity 1* and *Demonstration 1*).
2. Free halogen atoms (seven outer valence electrons) are one electron short of an eight-electron noble gas configuration. The atoms dimerize ($2X \rightarrow X_2$) or act as very strong oxidants ($X + e^- \rightarrow X^-$) to complete the octet of electrons.
3. Diatomic halogens are fairly strong oxidants ($X_2 + 2e^- \rightarrow 2X^-$; with $F_2 > Cl_2 > Br_2 > I_2 > At_2$). The reverse reaction can be obtained electrochemically or by stronger oxidizing agents. These reactive elements have characteristic properties, *e.g.*, at room temperature they exist as gases (fluorine and chlorine), a liquid (bromine), and solids (iodine and astatine) with colors ranging from light and medium yellow-greens for fluorine and chlorine through deep red for bromine to almost black with a metallic luster for iodine—although its vapor is a rich violet color (see *Laboratory Activity 2* and *Demonstrations 1b, 4*).
4. Halide ions (X^-) have noble gas electron configurations and are found in nature as stable crystalline solids (salts), that, with few exceptions, are soluble in water, are colorless unless colored by the cation component, and are used to form strong acids (except fluoride).
5. Halogens, except fluorine, form oxoanions (XO_n^-) that are highly reactive and can serve as bleaching agents and disinfectants similar to the elements themselves. Oxyhalogen ions provide another way for electron octet formation. These anions formally contain halogen atoms in positive oxidation states, which have even fewer valence electrons per halogen atom than in the free element. This is consistent with the fact that they are even stronger oxidants than are halogens.
6. Organic halogen compounds are rare in nature, although many useful and stable ones have been synthesized. They can be solids, liquids, or gases; some form very stable polymers. Halogens in these organics are covalently bonded to carbon, making organic halogen compounds inert, except in the presence of irradiation, heat, or catalysts. Unfortunately, many are highly toxic, and the stability of others is causing environmental problems.
7. Halogen elements provide trends that can be extended elsewhere in the Periodic Table. These include, but are not limited to, trends in oxidizing strength, atomic and ionic sizes, completion of the octet of electrons by sharing electrons or forming anions or oxoanions, and trends in electronegativities (see *Laboratory Activity 2* and *Demonstration 2*).

RELATED CONCEPTS

1. Redox (Oxidation-reduction concepts can be taught concurrently with this descriptive module.)
2. Acids and bases
3. Atomic structure, including ions
4. Bonding (electron-pair sharing and ionic aggregates in salts—the gas-to-solid trend can also be used in considering van der Waals or London dispersion forces)
5. Formula writing (nomenclature)
6. Equation writing and balancing
7. Electrochemistry (specifically, electron donation at the cathode and electron removal at the anode)
8. Solutions (one species dispersed in another as well as salts dissolved as solvated ions)
9. Periodicity

RELATED SKILLS

1. Ability to read carefully and follow instructions precisely.
2. Dexterity to handle and shake potentially hazardous solutions in small test-tubes and to handle a hot test-tube.
3. Arithmetic skills necessary for writing formulas and balancing equations.
4. Stoichiometry problems and quantitative laboratory activities should be added if this material is deferred until late in the year. (Representative sources for such quantitative material are listed at the close of this module.)

PERFORMANCE OBJECTIVES

Following their study of halogens, students should be able to:

1. identify halogens as a distinct family of elements.
2. describe the highly reactive nature of halogens.
3. describe how to prepare halogens electrochemically or chemically from halide melts of halide solutions.
4. identify the electron configuration of a halogen.
5. use electron configurations of halogen elements to explain why they dimerize and act as oxidants.
6. list halogens in order of increasing strength as oxidizing agents.
7. identify the characteristic properties of halogens.
9. recognize that halogens, except for fluorine, form oxyanions that are highly reactive and serve as bleaching agents and disinfectants.
10. demonstrate, with a Lewis diagram, how a halogen can complete its octet by forming an oxoanion in which the halogen has a positive oxidation state.
11. identify halogen-containing organic compounds.
12. explain, using the fact that halo-organic compounds are stable and thus desirable in applications, why halo-organic compounds pose an environmental problem.
13. use halogens as the basis for a confirmation of the periodic law.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Production and Chemistry of Chlorine

Introduction

Halogens represent a very reactive family of elements. One of the most common uses for halogens is as oxidizing agents.

Purpose

To prepare chlorine gas from common household bleach and use it to oxidize various materials.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Chlorine gas is highly corrosive and thus must *not* be allowed to enter the laboratory atmosphere. For this reason all work should be done in a properly operating fume hood. It is possible to detect the odor of chlorine at 3.5 ppm; chlorine is toxic at 1000 ppm.
3. Work toward the rear of the hood to avoid a backdraft of fumes from the front of the hood.
4. Be sure to empty carefully all three chlorine gas generator bottles into the NaOH wash solution when you complete the laboratory activity.
5. 12 M HCl is very corrosive and must be handled with care and dispensed in the hood.
6. When heating the steel wool in Step 6b be careful not to heat the test-tube and steel wool too strongly to avoid either melting the test-tube or igniting the steel wool.
7. Any substances spilled on your skin or clothing should be immediately washed off with large amounts of water and the incident should be reported to your teacher.
8. Dispose of all as your teacher directs.

Procedure

Part I. Preparation of Chlorine Gas

1. Obtain four wide-mouth bottles and one stopper fitted with a gas delivery tube. Place 70 mL of 2 M NaOH washing solution into one bottle (see Figure 1).
2. In all subsequent steps be sure to avoid splashing the sides of the bottles while adding the bleach and acid. Place 20 mL of commercial bleach into one bottle. Add 5 mL of concentrated HCl to the bleach and *immediately* insert the stopper fitted with gas delivery tube. Submerge the free end of the glass tube in the NaOH washing solution.
3. After a few seconds the bottle fitted with the stopper will be filled with chlorine gas, which you can then use in the tests.

Part II. The Oxidizing Power of Chlorine

Each of the following steps requires a fresh bottle of chlorine. Use the first bottle in Step 4, prepare another bottle in the manner described in Steps 1 through 3 for Step 5, and then yet another for Step 6. Cover the bottles with watch glasses or flat glass plates.

4. Obtain two strips of denim or other dyed cloth. Wet one strip of cloth with tap water; leave the other one dry. Remove the stopper and suspend each strip over the lip of the bottle filled with chlorine gas, making sure the strips do not touch each other. Cover the bottle. Record your observations.
5. a. After you have prepared a new bottle of chlorine gas, obtain a strip of white paper. Write on it with pen, ordinary pencil, and various colored felt-tipped markers. Remove the stopper and suspend this paper in the bottle, once again covering the bottle with a watch glass or glass plate. Try other samples such as a strip of newsprint or a flower petal. Record your observations.
   b. Repeat Step 5a with the same items moistened with tap water. Record your observations.
6. a. Place a small amount of steel wool into a new bottle of chlorine gas; quickly cover the bottle. Record your observations.
   b. Place a small (1-cm diameter) ball of steel wool into a clean, dry 15 x 150-mm test-tube and, holding the test-tube with a test-tube holder, heat the tube and steel wool in a flame. Once the steel wool is hot, remove the cover from the bottle of chlorine gas used in Step 6a and quickly "pour" the steel wool into the bottle; replace the cover. Record your observations.
7. To clean up, remove the solids from the bottles (steel wool, cloth, paper, and other tested items) with forceps and dispose of as directed by your teacher. Carefully and slowly pour the entire contents of the three chlorine gas generator bottles into the bottle containing 70 mL of NaOH wash solution. Pour the entire contents down the drain in the fume hood, while flushing with plenty of water. Then carefully rinse all bottles with tap water three times.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis

1. Which strip of cloth—wet or dry—reacted more with chlorine? On what observation did you base your answer?
2. Which marks written on the paper reacted with chlorine? On what observation did you base your answer?
3. Which piece of steel wool—hot or room temperature—reacted to a greater extent with chlorine? On what observation did you base your answer?

Implications and Applications

1. Write a balanced equation representing the reaction of bleach solution with acid. Assume the bleach solution is $NaClO(aq)$.
2. Why is it important to keep the sides of the bottles dry?
3. Provide reasons for your observation regarding the reactivity of wet *vs.* dry materials.

4. Was there any pattern to the reactivity of the inks? Can you make any generalization about their reactivity toward chlorine?

   How do you account for the behavior of the pencil mark on the paper?

5. a. Why did one piece of steel wool react more vigorously than the other? Did you expect this?

   b. Why did you not just heat the steel wool in the flame directly?

6. Write a balanced equation for the reaction of chlorine with steel wool, assuming the steel wool is pure iron.

7. Would you expect fluorine to react similarly to chlorine in the above tests? Why?

8. Would you expect bromine to react similarly to chlorine in the above tests? Why?

Chlorine Gas Preparation

The excess chlorine gas is absorbed into NaOH solution rather than into air. [Franz and Malm. (1968, 1969). *Fundamental experiments for college chemistry* (2nd Ed.). San Francisco, CA: Freeman.]

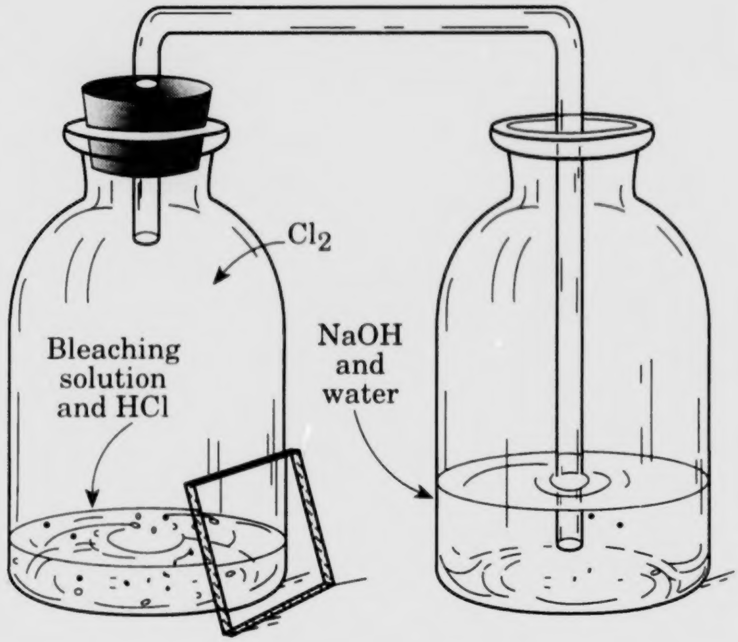


Figure 1. Apparatus for chlorine generation.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Production and Chemistry of Chlorine

Major Chemical Concept

This is an introductory laboratory activity, designed to be descriptive in nature, involving the reactivity of chlorine gas.

Level

Activity appropriate for basic, general, and honors students.

Expected Student Background

The major prerequisite for this laboratory activity is the ability to follow written instructions, make observations, and handle hazardous materials safely. You may choose to include this activity early in the year, since very little chemical knowledge is required.

Related concepts somewhat depend upon when this activity is used and what principles are being developed. Related concepts needed for understanding this activity include atomic structure, ions, formula writing, and equations. The activity is useful in developing an understanding of oxidation-reduction and periodicity.

Time

While the time to complete the activity depends on the availability of hood space and the number of students trying to use each hood, work can be completed in one 45-min period. Teacher preparation time will be about one hour, provided the glass tubing is already prepared. If not, then about a half-hour extra is required.

Safety

1. If insufficient hood space is available, consider conducting this activity as a demonstration. The chlorine is generated and stored in the hood; you then carry individual gas bottles (covered) back to the demonstration bench as needed. The bottles are *only* uncovered long enough to insert materials and then *immediately* recovered. Items to be investigated can be taped to other cover glasses, which then replace the original cover glasses.
2. Be certain the laboratory has adequate ventilation and is vented to outside of the school before you do this activity. The NaOH traps are very effective in preventing chlorine from entering the atmosphere.
3. Allow each student adequate room in the fume hood. Crowding can lead to accidents. The need for a burner in Step 6b means that only two students should work in a normal 4-foot hood.
4. An acid pump is recommended for dispensing the 12 M HCl to avoid the hazard of spills. Alternatively, a buret makes a very safe dispenser for small amounts of acid if you lack an acid pump. You must cover, but not seal, the top of the buret; students should still dispense the acid into a graduated cylinder. The reason for this is that it will be quicker and safer than trying to use buret markings to determine the volume and, more importantly, the acid must be added to the bleach quickly since the reaction is so rapid. Recognize, however, that the buret will need to be refilled often if you are supplying a large class.
5. *CAUTION*: Chlorine bleaches and ammonia-containing cleansers should never be mixed, since they react to form very toxic chloramine (NH_2Cl). *No bottles of aqueous ammonia should be present on the benches during this activity. An inadvertent error could cause a serious problem.*

Materials (For 24 students working in pairs)

48 Wide-mouth bottles, 250-mL capacity
12 Rubber stoppers fitted with glass tubes
Chlorine bleach, such as Clorox™
2 M Sodium hydroxide, NaOH, 1 L (80 g diluted to 1 L)
12 M Hydrochloric acid, HCl, 250 mL
12 Graduated cylinders, 10- and 100-mL sizes
36 Pyrex watch glasses or flat glass plates to cover the bottles
12 Strips of denim and/or other dyed cloth (used or prewashed so it wets easily)
12 Strips of newsprint
12 Flower petals
Other items to be bleached—add your own items to the list, *but test them first!*
A small amount of fine steel wool. (*NOTE: Inexpensive, commercial steel wool is often oil coated and gives poor results.*)
12 Test-tubes, 15- x 150-mm
12 Test-tube holders
12 Burners and lighters
12 Pairs forceps

Advance Preparation

Complete the activity yourself with the bleach you intend to use. It would be wise to use a fresh bottle of bleach. If the bleach is old you may not get much reaction, and thus not much chlorine. Should you find yourself without any bleach, consult the school custodian.

Pre-Laboratory Discussion

Insure that students understand the safety instructions. Demonstrate proper placement of the stopper in the chlorine generator and the glass tube in the NaOH solution. Also focus on the difference between chlor*ine* and chlor*ide*.

Teacher-Student Interaction

Monitor the generation of gas in the hood. This way you can prevent the release of unwanted gas into the atmosphere and ensure that things are working properly.

Expect students to want to test the reactivity of chlorine with such unorthodox items such as hair, gum, or anything else that they can find. *This must be prevented!*

Anticipated Student Results

Data Analysis

(These answers correspond to *Data Analysis* Questions 1, 2, and 3.)

1. **Step 4**: Wet strips of cloth will discolor more quickly and completely than the dry ones. From this observation it is concluded that the wet strips reacted more with the chlorine.
2. **Step 5**: The blue inks will turn brown. Felt-tipped marker behavior must be determined by trial. Do this yourself. The pencil mark will not discolor. These observations help determine which inks reacted more with the chlorine.
3. **Step 6**: Cool steel wool will not react; hot steel wool will react vigorously with evolution of much brown smoke. From these observations it can be concluded that the hot steel wool reacted more vigorously with chlorine.

Answers to Implications and Applications

1. $2HCl(aq) + NaClO(aq) \rightarrow Cl_2(g) + NaCl(aq) + H_2O(l)$
2. The sides must be dry so the strips of tested material are not able to react with the bleach or acid—the observed results are thus due only to reaction with chlorine gas.
3. The wet cloth reacts faster and more completely than does the dry cloth because the gas can dissolve in the water and be brought into chemical contact with the dye.
4. It is expected that some inks will be more reactive than others. Therefore, you will need to determine the answer to this question by testing the actual inks used. (We anticipate that the wet paper, and "wetter" inks should be more reactive than the dry ones.)

   The pencil "lead" is actually graphite (carbon), and carbon is not reactive with chlorine at room temperature. (It is only reactive with chlorine at very high temperatures.)
5. a-b. The cool steel wool (iron) does not react rapidly due to the activation energy required. Hot steel wool possesses the needed activation energy. The steel wool was not heated directly in the flame because it would be oxidized in the flame—there could be some confusion regarding what caused the reaction.
6. $3Cl_2(g) + 2Fe(s) \rightarrow 2FeCl_3(s)$. Iron in the III oxidation state is expected because chlorine is an oxidizing agent, although above 500 °C $FeCl_3$ begins to spontaneously reduce to $FeCl_2$:

   $$2FeCl_3(s) \rightarrow 2FeCl_2(s) + Cl_2(g)$$
7. Yes. It would be expected, based upon element positions on the Periodic Table, that fluorine would be even more reactive than chlorine toward the test materials. Note that the following side reaction also occurs with fluorine:

   $$2F_2(g) + 2H_2O(l) \rightarrow O_2(g) + 4HF(g)$$
8. It would be expected, based upon positions in the Periodic Table, that bromine would be less reactive than chlorine toward all test materials.

Post-Laboratory Activities

Allow students ample time to answer the questions before discussing the laboratory activity.

Possible Extensions

1. You may repeat Steps 4 through 6 with chlorine bleach and compare the results with those involving chlorine gas. Note that the oxidizing agent in bleach is the hypochlorite (ClO^-) ion.
2. You may also repeat Steps 4 through 6 with nonchlorine bleach and compare results with those of the chlorine gas and chlorine bleach.
3. a. If this activity comes after a study of kinetics, students can understand that the vigor of an oxidation-reduction reaction can depend on the concentrations of reactants. For example, to illustrate redox and the concept of relative oxidation strengths, heat the steel wool directly in the flame and compare the reaction to steel wool in chlorine. This is evidence that chlorine is more reactive than the oxygen in the air. (Be sure to compare the reactivities with the same grade (fineness) and compactness of "wad.")

b. To further reinforce this concept, point out that oxygen in air does not oxidize the dye in their clothing or any other materials they tested.

c. Recognizing that the Cl_2 concentration in the bottle is higher than that of O_2 in air, you could drift into a discussion that includes more than you had probably intended. The whole concept of concentration effects and their importance in reaction kinetics is probably beyond most students. You may recall, however (even though your students will not) that the concentrated oxygen environment of the first *Apollo* spacecraft was blamed for the fire that killed three men on the launch pad and resulted in the destruction of much of the space capsule contents.

Assessing Laboratory Learning

Written Examination

1. Write equations to represent the reactions of chlorine gas with the materials tested. What is the main feature of all of the reactions?
2. Comment on the reactivity of chlorine gas and predict how fluorine gas, bromine vapor, or iodine vapor would react with the same materials.

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: *Relative Reactivity of Halogens and Halides*

Introduction

The halide anions and halogen elements are appreciably different in their tendencies toward oxidation and reduction.

Purpose

To determine the relative ease of oxidation of chloride, bromide, and iodide ions and the relative oxidizing strengths of their respective elements.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Do not inhale vapors from the halogens or cyclohexane.
3. All reagents should be placed in the fume hood and dispensed from there.
4. Do not interchange droppers used to dispense the solutions.
5. No operating burners or other flames should be present in the laboratory during this laboratory activity.
6. Any chemicals spilled on your skin or clothing should be immediately washed off with large amounts of water; report the incident to your teacher.
7. Do not cover the test-tubes with your thumb to mix the reagents—use a cork instead. Corks should not be interchanged and should be left loose on the test-tubes after mixing.
8. Read the labels carefully; *e.g.*, chlor*ide* *vs.* chlor*ine*.
9. Dispose of the materials as your teacher directs.

Procedure

1. Obtain nine small, clean test-tubes. They need not be dry since aqueous solutions will be placed in them. With a wax crayon, label them from 1 to 9. To one test-tube, add 1 mL water. Mark the level with a wax crayon. Add two successive milliliters water and mark the tube at the 2- and 3-mL levels. Using this test-tube as a guide, mark the other eight test-tubes in a similar fashion.
2. Take Tubes 1-6 to the hood.

   In Tube 1 place 1 mL chlorine water, $Cl_2(aq)$;
   in Tube 2 place 1 mL bromine water, $Br_2(aq)$;
   in Tube 3 place 1 mL iodine water, $I_2(aq)$;
   in Tube 4 place 1 mL potassium chloride (KCl) solution;
   in Tube 5 place 1 mL potassium bromide (KBr) solution; and
   in Tube 6 place 1 mL potassium iodide (KI) solution.

   (Remember, KCl in aqueous solution consists of K^+ ions and Cl^- ions. KBr and KI are also dissociated in aqueous solution.)
3. Add a few drops of cyclohexane to the first tube. Note whether the cyclohexane floats or sinks to the bottom. Use this observation to determine the position of the cyclohexane layer in all succeeding trials.

4. Add 1 mL cyclohexane to Test-Tubes 1-6. Stopper, shake, and loosen stopper. Record the colors of the top and bottom layers in all test-tubes. (Colors in the cyclohexane layers are due to the extraction of chlorine, bromine, or iodine into the organic layer.)
5. Save and use Tubes 1-6 for comparison later.
6. Take Tubes 4-9 to the hood.

   In Tubes 4 and 7, place 1 mL KCl solution;
   in Tubes 5 and 8, place 1 mL KBr solution; and
   in Tubes 6 and 9, place 1 mL KI solution.
7. Place 1 mL $Cl_2(aq)$ in Tubes 5 and 6;
   place 1 mL $Br_2(aq)$ in Tubes 4 and 9; and
   place 1 mL $I_2(aq)$ in Tubes 7 and 8.

   Shake each test-tube after stoppering it as above. Then remove the corks and add 1 mL cyclohexane to each tube (4-9). Re-stopper, shake the test-tubes to observe the layering of the halogen that is present in the tube after the initial shaking. Prepare a data table (see Figure 2). Record the colors in both layers of each test-tube.
8. Show your data table and test-tubes to your teacher before discarding the tube contents in the appropriate waste container. Rinse and clean the tubes thoroughly and return them to the appropriate place in your laboratory.
9. Thoroughly wash your hands before leaving the laboratory.

Data Analysis

1. From the colors in Tubes 4-9 and the reagents you added, determine in which test-tubes a chemical reaction occurred. (For example, if the color of the cyclohexane layer in Tube 4 is similar to that in Tube 2, no reaction occurred between bromine and the chloride ion. However, if the color in the cyclohexane layer of Tube 4 is similar to that in Tube 1, bromine *has* reacted with the chloride ion to produce chlorine and the bromide ion.)
2. Record your results (color) in a table such as the one shown. Also draw each tube and use colored pencils to record your results.

	Cl^-	Br^-	I^-	None	
Cl_2	▨	(5)	(6)		Cyclohexane layer
	▨	(5)	(6)	(1)	Water layer
	▨			Control	Reaction?
Br_2	(4)	▨	(9)	(2)	Cyclohexane layer
	(4)	▨	(9)	(2)	Water layer
		▨		Control	Reaction?
I_2	(7)	(8)	▨	(3)	Cyclohexane layer
	(7)	(8)	▨	(3)	Water layer
			▨	Control	Reaction?

Figure 2. Data table format. (Numbers in parentheses refer to the test-tube number.)

Implications and Applications

1. If you were given an unknown solution containing one of the halide ions (Cl^-, Br^-, or I^-), what single, simple test could you use to determine which ion was in the solution? Describe the procedure and results expected for each of the three ions.
2. Rank the three halogen elements used in terms of their relative oxidizing ability, from the strongest oxidizer to the weakest.
3. How does the order of the halogens specified in Question 2 compare with their relative positions in the Periodic Table? Based on its position in the Periodic Table, would you expect fluorine to be a stronger or weaker oxidizing agent than the other halogen elements studied here?
4. Write a net ionic equation for each reaction that occurred in your trials.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: Relative Reactivity of Halogens and Halides

Major Chemical Concept

Halide ions and halogens differ in their tendencies toward oxidation and reduction.

Level

Activity appropriate for basic, general, and honors students.

Expected Student Background

Related concepts needed for this exercise include oxidation-reduction, ions, formula writing, equations, and periodicity. Required laboratory skills include following directions fully and the ability to handle potentially hazardous materials.

Time

40 min of work time—longer if insufficient hood space is available.

Safety

1. Read the *Safety* section in the student procedure.
2. Place all reagents in dropping bottles to facilitate dispensing by students. We recommend plastic bottles with nonrubber dropper tops for $Cl_2(aq)$, $Br_2(aq)$, and $I_2(aq)$. If rubber dropper tops are used, check the caps and replace any that have cracks. *Do not* store halogen solutions in bottles with rubber dropper tops.
3. Place all solutions in scrupulously clean bottles.

Materials (For 24 students working in pairs)

See previous safety suggestions regarding reagents and reagent bottles.

12 Test-tube blocks or racks
108 Test-tubes, 13- x 100-mm
108 Corks to fit test-tubes
Cyclohexane or mineral spirits (paint thinner), 150 mL
0.1 M Potassium chloride, KCl, 100 mL (0.75 g KCl per 100 mL solution)
0.1 M Potassium bromide, KBr, 100 mL (1.2 g KBr per 100 mL solution)
0.1 M Potassium iodide, KI, 100 mL (1.7 g KI per 100 mL solution)
Chlorine water, Cl_2 (aq), 100 mL
Bromine water, Br_2 (aq), 100 mL
Iodine water, I_2 (aq), 100 mL

The 0.1 M solutions of KCl, KBr, and KI are made by dissolving 0.75 g potassium chloride, 1.2 g potassium bromide, and 1.7 g potassium iodide, respectively, in sufficient distilled water to make up 100 mL solution. This is enough for 20 student groups. The X_2 solutions are commercially available chlorine water, bromine water, and iodine water.

Waste disposal bottles to hold about 100 mL waste solutions per student group should be available (see waste disposal information in the *SourceBook Safety* section).

Advance Preparation

1. Chlorine water solution cannot be stored for extended periods. It has a very short shelf-life and should be tested just before students are to start the activity—*i.e.*, check with KBr solution to ensure that enough bromine is liberated to be extracted into the cyclohexane layer. (The formation of a yellow color in the aqueous layer is not conclusive.) In an emergency, chlorine water can be prepared by setting up the apparatus shown in *Laboratory Activity 1* of this module and bubbling the generated chlorine into water.
2. Inspect the KI solution for decomposition. Even if no coloration is visible, several milliliters of KI can be tested with a few drops of starch solution. A blue color indicates that a fresh solution is needed. If corks are reused from class to class, be sure they are washed thoroughly.
3. Be sure to complete the laboratory activity yourself before allowing students to attempt it.
4. Tell students to shake test-tubes for a fairly long time.

Pre-Laboratory Discussion

Insure that students understand all safety instructions. Consider a brief review of related concepts (see *Expected Student Background*). Stress the nomenclature distinction between halide ions (such as chlor*ide*, Cl^-) and halogens (such as chlor*ine*, Cl_2).

Teacher-Student Interaction

The teaching value of this laboratory activity can be increased if you move from group to group and ask students about the Part 1 extractions to ensure that they understand the difference between an *extraction* and a *chemical reaction*. Confirm that students follow safety instructions provided. During Part 1, stress the importance of allowing the aqueous components to react prior to extraction. Students may be tempted to mix all three components together, which, unfortunately, would minimize the chance of complete reaction in a short time span and may generate ambiguous results. Students should shake the cork-stoppered test-tubes *thoroughly* to promote extraction.

Anticipated Student Results

1. **Procedure Step 3**: The cyclohexane layer remains above the water layer.
2. **Procedure Step 4**:

   Tube 1: top (cyclohexane) layer: yellow; bottom (water) layer: colorless

   Tube 2: top (cyclohexane) layer: orange; bottom (water) layer: light yellow

   Tube 3: top (cyclohexane) layer: violet; bottom (water) layer: light yellow

   Tube 4: top (cyclohexane) layer: colorless; bottom (water) layer: colorless

   Tube 5: top (cyclohexane) layer: colorless; bottom (water) layer: colorless

   Tube 6: top (cyclohexane) layer: colorless; bottom (water) layer: colorless
3. **Steps 6 and 7**: See Data Table

	Cl^-	Br^-	I^-	None	
Cl_2	▨	*Orange* (5)	*Violet* (6)	*Yellow*	Cyclohexane layer
		Lt. yellow (5)	*Lt. yellow* (6)	*Colorless* (1)	Water layer
		Yes	*Yes*	Control	Reaction?
Br_2	*Orange* (4)	▨	*Violet* (9)	*Orange* (2)	Cyclohexane layer
	Lt. yellow (4)		*Lt. yellow* (9)	*Lt. yellow* (2)	Water layer
	No		*Yes*	Control	Reaction?
I_2	*Violet* (7)	*Violet* (8)	▨	*Violet* (3)	Cyclohexane layer
	Lt. yellow (7)	*Lt. yellow* (8)		*Lt. yellow* (3)	Water layer
	No	*No*		Control	Reaction?

Figure 3. Sample data table.

Answers to Implications and Applications

1. Add chlorine water to the solution containing the halide ion and shake. Add cyclohexane and shake again. A yellow color in the cyclohexane layer indicates no reaction occurred—the anion must have been chloride. However, an orange layer indicates formation of bromine—the anion must have been bromide. A violet layer indicates iodine—the anion would be iodide in this case.
2. Chlorine is the strongest oxidizing agent, bromine is intermediate, and iodine is the weakest oxidizing agent.
3. The higher the halogen is located in the Periodic Table, the stronger its character as an oxidizing agent. On this basis, fluorine would be expected to act as a stronger oxidizing agent than chlorine—which is true.
4. **Step 4**: No chemical reactions take place.

   Steps 6 and 7:

$$\begin{array}{rcll} Cl_2 + 2Br^- & \rightarrow & 2Cl^- + Br_2 & \text{(Tube 5)} \\ Cl_2 + 2I^- & \rightarrow & 2Cl^- + I_2 & \text{(Tube 6)} \\ Br_2 + 2I^- & \rightarrow & 2Br^- + I_2 & \text{(Tube 9)} \end{array}$$

Post-Laboratory Activity

Help develop the *Answers to Implications and Applications* Question 1 and then demonstrate the reaction of chlorine water with an unknown halide ion solution.

Possible Extensions

1. Each student could be given an unknown halide ion solution and asked to determine which halide ion it contains, again using the procedure developed in Question 1.
2. The relative reactivity of halide ions as reducing agents could be explored by more advanced students. Iron(III) and copper(II) are allowed to react with iodide and bromide ion solutions. The iodide ion reduces both metal ions—to iron(II) and copper(I), respectively. The bromide ion is unable to reduce either metal ion.

Assessing Laboratory Learning

Laboratory Practical

Each student could be given an unknown halide ion solution and asked to determine which halide ion it contains, again using the procedure developed in Implications and Applications Question 1.

Demonstration Examination

Same as laboratory practical, but you would demonstrate the tests on one or more "unknowns" with students observing the results and identifying the ion in the unknown or unknowns.

Written Examination

1. Write net ionic equations for the reaction between
   a. Cl_2 and Br^- *[*$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$*]*
   b. Cl_2 and I^- *[*$Cl_2 + I^- \rightarrow I_2 + 2Cl^-$*]*
   c. Br_2 and I^- *[*$Br_2 + 2I^- \rightarrow I_2 + 2Br^-$*]*
2. Consider the data table (see Figure 4). In which trials did a reaction occur? Explain your reasoning for each answer.

Data for combinations of Br_2 and halide ions

	Cl^-	Br^-	I^-	
Br_2	*Orange*	*Orange*	*Violet*	Cyclohexane layer
	Lt. yellow	*Lt. yellow*	*Lt. yellow*	Water layer
				Reaction?

Figure 4. Colors observed in bromine-halide systems.

[TEACHER NOTE: Bromine has not reacted with Cl^- *or* Br^-*, since* Br_2 *color appears in organic layer.* Br_2 *has reacted with* I^- *to give* I_2*.]*

Note that another row or column could be used for this question.

3. Consider another halogen element X. An organic solvent added to an X_2 solution exhibits a colorless organic layer by itself, even when shaken vigorously. When X_2 solution is added to solutions of chloride, bromide, and iodide ions, the results shown below are observed.

Data for combinations of X_2 and halide ions

	Cl^-	Br^-	I^-	
X_2	*Yellow*	*Orange*	*Violet*	Cyclohexane layer
	Colorless	*Lt. yellow*	*Lt. yellow*	Water layer
				Reaction?

Figure 5. Unknown halogen sample data table.

Where does this halogen fit in the Periodic Table relative to Cl, Br, and I? *[TEACHER NOTE: This is undoubtedly fluorine, since* Cl_2*,* Br_2*, and* I_2 *have been produced. A similar table with a fictitious element or with astatine could be developed.]*

Suggestions for Other Laboratory Activities

A quantitative laboratory activity might be advisable if this material is presented late in the school year—provided you perform demonstrations that cover the principles involved in the laboratory activities presented here. One quantitative activity is the "Ferric Ion/Iodide Ion Reaction" of the *Doing Chemistry* Videodisc Set, distributed by the Education Division, American Chemical Society, 1155 16th Street, N.W., Washington, DC 20036.

DEMONSTRATIONS

Demonstration 1: Halogen and Halide Reactivity

Option A

The reactivity of a halogen *vs.* relative nonreactivity of the halide ion:

Safety

Follow the standard safety procedures for any demonstration. For this particular demonstration, be sure to:

1. Wear protective goggles and apron.
2. Wash off any chemicals spilled on your skin or clothing with large amounts of tap water.
3. Dispose of chemicals by dissolving them in tap water and washing them down the drain with copious amounts of tap water.

Materials

Sodium chloride (table salt) solution (any concentration) in a beaker
Chlorine water in another beaker
Strips of denim or other cotton cloth

Directions

Dip a strip of cotton denim into an aqueous solution of sodium chloride. Dip another strip into a fresh chlorine water solution. The strips of cloth should be large enough to be seen by all students. Pass the strips around the class *after* washing the strips in water to remove excess sodium chloride and chlorine.

(This simple demonstration can set the stage for *Laboratory Activity 1.*)

Option B

As a counterintuitive demonstration, solutions of potassium bromide and potassium iodide can be mixed with solutions of iron(III) and copper(II) chlorides.

Materials

1 M Potassium bromide, KBr, 10 mL (1.2 g KBr per 10 mL solution)
1 M Potassium iodide, KI, 10 mL (1.7 g KI per 10 mL solution)
1 M Copper(II) (cupric) chloride, $CuCl_2$, 10 mL (1.7 g $CuCl_2 \cdot 2H_2O$ per 10 mL solution)
1 M Iron(III) (ferric) chloride, $FeCl_3$, 10 mL (2.7 g $FeCl_3 \cdot 6H_2O$ per 10 mL solution)
8 Small Petri dishes on overhead projector (image quality is best with plastic Petri dishes, intermediate with glass Petri dishes, and poorest with small beakers)

Directions

Pour a layer of the four respective solutions thick enough to see the color in four Petri dishes as controls (see Figure 6). Then pour equal volumes of the Fe^{3+} solution in two remaining dishes and equal volumes of Cu^{2+} solution in the final two dishes. Add equal volumes of potassium bromide to one dish containing Fe^{3+} and one containing Cu^{2+}. Note any color changes. Now add equal volumes of potassium iodide solution to the second dish of Fe^{3+} and Cu^{2+} solutions. Observe the color changes. (Iodide is able to reduce these ions to Fe^{2+} and Cu^{+}, respectively, with concurrent changes in the brown color of iodine in water.) As an extra touch, the brown solutions can be transferred by pipets to test-tubes. Add cyclohexane, stopper, and shake to transfer the iodine to the cyclohexane layer. The violet color can be observed on the overhead projector if the cyclohexane layers are transferred to Petri dishes.

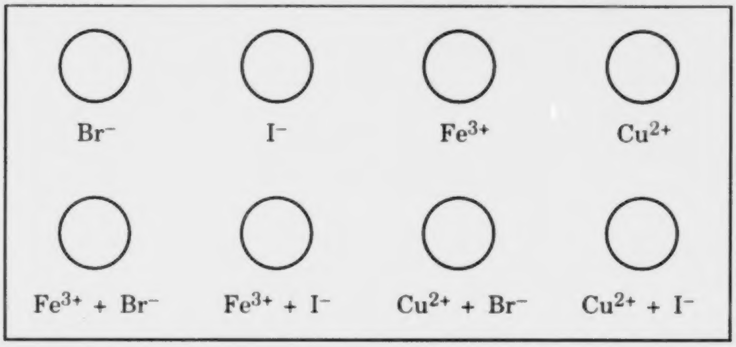


Figure 6. Arrangement of Petri dishes and labels on overhead projector stage.

Alternatively, the demonstration can be presented on a larger scale with more dilute solutions from a demonstration bench at the front of class. In this case, color changes are more readily observed if a sheet of white posterboard is placed behind the solutions.

This demonstration can be made an extension of *Laboratory Activity 2.* This develops a more thorough understanding of relative oxidizing and reducing abilities of redox couples as well as better understanding of halogen chemistry.

Demonstration 2: Chlorine Production by Electrolysis of a Chloride Solution

Introduction

$CuCl_2(aq)$ is electrolyzed rather than $NaCl(aq)$ since it removes possible confusion inherent in simultaneous production of $H_2(g)$ and $Cl_2(g)$.

Safety

Follow the standard safety procedures for any demonstration. For this particular demonstration, please be sure to:

1. Wear protective goggles and apron throughout the demonstration.
2. Wash off any chemicals spilled on your skin or clothing with large amounts of tap water.
3. Dispose of chemicals by dissolving them in tap water and washing them down the drain with copious amounts of tap water.

Materials

1 M Copper(II) chloride, $CuCl_2$, 50 mL (8.5 g $CuCl_2 \cdot 2H_2O$ per 50 mL solution)
Petri dish
2 Mechanical pencil "leads" (about 6 cm long; graphite) or larger diameter graphite rods
2 1.5-V Dry cells connected in series with alligator clip leads, or a 9-V battery wrapped with tape and connectors wired to alligator clips
2 Small pieces (0.5 x 3 cm) of dyed cotton and/or litmus paper (litmus paper preferred since many dyes are bleach proof)
Overhead projector

Directions

Place the Petri dish containing 1 M $CuCl_2$ solution on the overhead projector. Disconnect the wire connecting the two cells in series. Connect the alligator clips to the pencil "lead" electrodes. Position the electrodes in the $CuCl_2$ solution so they are parallel and about 2 cm apart, with the top of the electrodes being supported by the rim of the Petri dish (see Figure 7). *Be sure that the electrodes do not contact each other during the demonstration.* (The graphite electrodes have very little resistance. If they touch, you will short the cells and create a possible hazardous condition.) About 2-3 cm of the electrodes should be submerged at an angle in the solution.

Alternatively, two graphite electrodes can be taped to a 9-V radio battery (pretaped to avoid shorting out of the electrodes through the case). The electrodes should be taped at an angle that allows 2-3 cm to be submerged in the solution.

The length of the electrodes should be visible on the projection screen. Reconnect the dry cells. You may or may not wish to identify the anode and cathode. After an initial induction time of about 20 seconds, ask students what they observe. *[Small bubbles should form at the anode and rise to the surface of the solution.]* Allow the electrolysis to continue for about 3-4 min. Call a student to the overhead projector and ask for a report on any apparent odor. Although only a fraction of a milliliter of Cl_2 gas has been produced, a distinct chlorine odor should be detectable near the overhead projector.

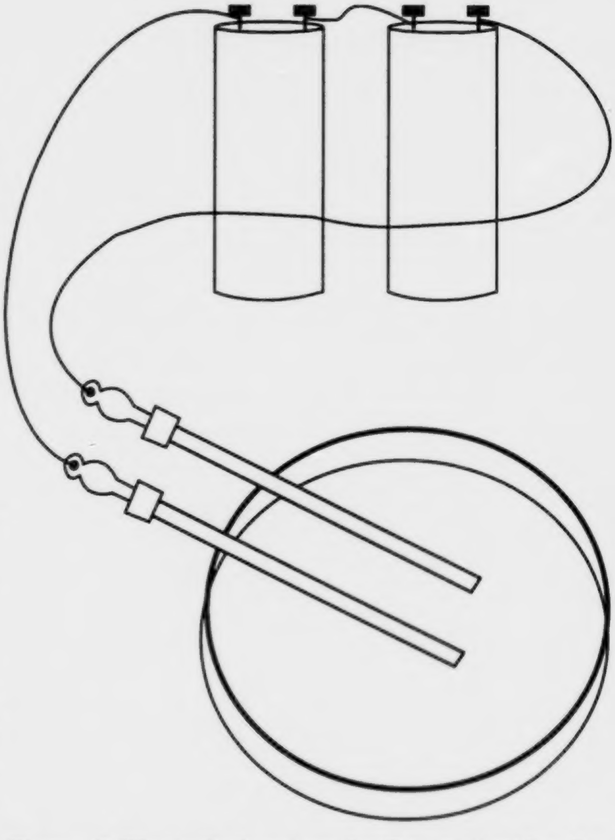


Figure 7. Electrolysis set-up for Demonstration 2.

Disconnect the wire connecting the two cells. Skewer the piece of dyed cloth or litmus paper with the tip of the anode (see Figure 8). Reposition the anode in the $CuCl_2$ solution as before, with the skewered part of the cloth/litmus paper submerged and the electrode beneath the cloth/litmus paper. A second piece of cloth/litmus should be partially submerged in the $CuCl_2$ solution away from the electrodes.

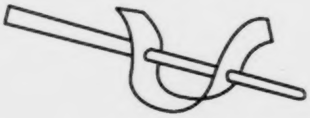


Figure 8. Dyed cloth or litmus paper attached to anode.

Reconnect the cells and permit electrolysis to occur for 2-3 min. Disconnect the wire connecting the cells and remove both pieces of cloth/litmus paper from the solution. Rinse the cloth/litmus in water and pass them around the room. Ask students to compare the pieces of cloth/litmus and to explain their observation. *[The piece of dyed cloth / litmus not attached to the electrode may be slightly discolored due to the $CuCl_2$ solution. The piece of dyed cloth / litmus skewered on the anode will be obviously bleached. This is secondary indication that the gas produced at the anode is chlorine. It is worth noting that litmus, a natural dye, works better than the dyed cloth.]*

Remove the cathode from the solution, rinse it in water and pass it around the room for students to observe. Ask students to explain their observations. *[Copper plating should be clearly visible on the cathode. The reaction* $Cu^{2+} + 2e^- \rightarrow Cu$ *takes place at the cathode.]*

A discussion of commercial production of Cl_2 by electrolysis of NaCl solutions could precede or follow this demonstration. Depending on when this activity is performed, you might elect to tackle the question of why Cu is plated at the cathode in this demonstration while H_2 is released at the cathode in the electrolysis of NaCl. *[This is because water is easier to reduce than are the sodium ions.]* Try to keep emphasis on Cl_2 production.

Demonstration 3: The Activity of HF(aq) as an Acid

Introduction

Hydrofluoric acid is a very active weak acid. It is classified as a weak acid due to its low ionization in aqueous solutions yet, seemingly paradoxically, it can etch glass.

Purpose

To use HF(aq) to etch glass and plastic and to compare the results.

Safety

Hydrofluoric acid is highly corrosive and thus must be handled with care. For this reason a paste form, available in some stained glass or art supply shops, is used. Do not allow your skin to come into contact with the paste. Flush the residues down the drain with plenty of water when finished.

Be careful not to drop the glass sample when it is passed around the room. Wear goggles and apron while performing this demonstration.

Materials

Small bottle or jar of commercial HF(aq) paste, with plastic applicator
Small piece of soft window glass, without sharp edges
Small piece of plastic
Tape for masking glass and plastic
Protective plastic sheet for desk top

Procedure

1. Prior to conducting the demonstration for the class, do the demonstration yourself, using scrap materials.
2. Prior to the demonstration, distinguish the oxidizing power of halogens (F_2 in particular) from the replacement reaction occurring in this demonstration.
3. Place a piece of tape across the middle of the glass plate. You may elect to be artistic and mask out a design.
4. Using a plastic applicator, smear a small amount of commercial HF(aq) paste across the entire glass plate including the tape.

5. Note the instructions on the container of HF(aq) paste. After a few minutes, rinse the glass with copious amounts of water. Remove the tape to display the etched glass.
6. Repeat Steps 3-5 with the piece of plastic.
7. Pass the well-rinsed pieces of glass and plastic around the room so students can observe the action of HF(aq) on the glass and the contrasting lack of reaction with the plastic.
8. Ask students to describe the difference in the glass and plastic surfaces where the HF(aq) was in contact with glass or plastic and where the tape covered the surface. *[Negligible change should be observed with the plastic.]* You can also ask students to write equations that represent the ionization of HF(aq) in aqueous solution:

   $$HF(aq) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$$

   and the equation representing the action of HF(aq) on glass (SiO_2):

   $$6HF(aq) + SiO_2(s) \rightarrow 2H_3O^+(aq) + SiF_6^{2-}(aq)$$

   Ask students to comment on the power of HF(aq) to etch glass and to suggest reasons for this behavior. *[The silicon to fluorine bond is more stable than the silicon to oxygen bond. Therefore, fluorine displaces oxygen in the glass structure. The frosted surface is the result of the once smooth glass surface becoming heavily pitted.]* Consider asking more able students to indicate why the HF(aq) paste did not react with the plastic. *[The bond strength for hydrogen to fluorine is about the same as the bond strength for carbon to hydrogen. The added steric hindrance associated with the smaller carbon atom (relative to silicon) together with the lack of a driving force for the reaction prevents any appreciable reaction being observed.]*

NOTE: If unavailable locally, glass etching cream can be obtained from Armour Products, Wyckoff, NJ 07481; (201) 847-0404. Call to determine a retail outlet in your area. Cost: about $6.00 for 3 oz.

Demonstration 4: Halogen Elements and Vapors

Option A

The sublimation of iodine makes a good demonstration.

Safety

Follow the standard safety procedures for any demonstration. For this particular demonstration, please be sure to:

1. Wear protective goggles and apron throughout the demonstration.
2. Wash off any chemicals spilled on your skin or clothing with large amounts of tap water.
3. Save the iodine for future demonstrations. Small amounts remaining on container surfaces can be washed from the vessels with scrubbing and then washed down the drain with copious amounts of tap water.

Materials

Plastic coffee can lid
Large beaker, size depends on size of coffee can plastic lid or cover
Small beaker filled with ice/water/salt mixture for cooling
A few iodine crystals, $I_2(s)$
Hot plate

Directions

Cut a hole in the coffee can plastic lid, allowing the small beaker to be suspended over the large beaker. Iodine crystals are placed in the large beaker, which is placed on the hot plate (low heat). Dark iodine crystals sublime as beautiful violet vapors and condense on the outer surface of the cold small beaker.

Option B

Demonstrate by textbook illustrations, by a photographic Periodic Table, or other media presentation the appearance of other elements and their vapors. Media sources are provided in the *Media* section.

Suggestions for Other Demonstrations

1. Other demonstrations are possible. See for example, Shakhashiri, *Chemical Demonstrations,* Volume 1:

   Demonstration 1.25: Reaction of Sodium and Chlorine
   Demonstration 1.26: Reaction of Antimony and Chlorine
   Demonstration 1.28: Reaction of Aluminum and Bromine
   Demonstration 1.29: Reaction of White Phosphorus and Chlorine
   Demonstration 1.30: Reaction of Red Phosphorus and Bromine

2. A number of oscillating reactions also contain halogen compounds, but details of these reactions are often "over the heads" of high school students. On the other hand, able students can be challenged by such reactions; c.f., Epstein, I. (1987). *Chemical and Engineering News, 65*(13), 24-36. Two overhead projector oscillating reaction demonstrations appropriate for this module are found in a short note by Kolb, D. (1988). *Journal of Chemical Education*, *65*(11), 1004.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. Where and in what form are halogens found in nature? *[Halogens are found as halide salts, often in solution, either in oceans or in subterranean brines, or as solid deposits on land. Insoluble calcium fluoride, and soluble alkali metal chlorides, bromides, and iodides are most common. Iodine has been found as the iodate in some calcium minerals, but known deposits have been largely used up. Iodine from seaweed was also a common source at one time.]*
2. Why aren't these elements found in free form in nature? *[Halogens are too reactive to be found in their free or elemental form in nature.]*
3. What processes are employed to obtain halide ions from natural sources? *[Calcium fluoride is dissolved in sulfuric acid to provide HF, which can be used as a source of metal fluoride salts by adding a metal hydroxide or carbonate to the HF. The soluble halide salts are typically dissolved and reprecipitated.]*
4. What processes are employed to obtain free halogens from natural sources? *[Fluorine and chlorine are typically obtained through electrochemical oxidation of their halides, either in aqueous media or in a melt. Bromine and iodine are typically made from oxidation of bromide or iodide, respectively, by chlorine.]*
5. What are some properties of halogen elements? *[Fluorine and chlorine are yellow-green gases, bromine is a deep red liquid, and iodine is a very deep violet (essentially black) lustrous solid, etc. For further elaboration, see an inorganic textbook that emphasizes descriptive chemistry, such as Greenwood and Earnshaw,* Chemistry of the Elements.*]*

6. How do chemical properties of halogen elements vary with their positions in the Periodic Table? *[For example, as the family is surveyed from fluorine to iodine, ionization energies decrease, electron affinities maximize at chlorine, but electronegativity decreases from fluorine on, radii increase, electrode potentials and oxidizing powers decrease. Also see Question 5.]*
7. What are some uses of halogens and halogen compounds in industry and in consumer products? *[Uses have been summarized in* Content in a Nutshell *and in* Links/Connections.*]*

Counterintuitive Examples and Discrepant Events

1. HF(aq) is a very reactive, weak acid. This does, at first glance, seem to be a contradiction. It is not. The great attraction that fluorine has for most other atoms is the cause of HF(aq) being a weak acid. This high attraction of fluorine for most other atoms gives rise to a very strong H—F bond that is not broken when HF dissolves in water. The designation of HF as a weak acid does not mean that it is unreactive, only that it does not ionize completely in water. Indeed, periodicity is confirmed by the great attraction between H and F—an attraction that is greater than H—Cl > H—Br > H—I (see *Demonstration 3*).
2. Iodide is a reactant in Option B of the *Halogen Reactivity* demonstration (Demonstration 1), and is thus possibly not "stable." This discrepant event is really nothing more than confirmation that Br^- is more stable to oxidation than is I^- and that I_2 is more stable to reduction than Br_2—confirmation of periodic trends illustrated in the laboratory activities.

Metaphors and Analogies

1. Halogens can be regarded as very "electron greedy" species. Their high electronegativities point out the fact that, in a covalent bond, they attract the shared pair of electrons aggressively. Indeed, if at all possible, a halide anion will form as the halogen seeks the bonding pair of electrons for itself. Family relationships involving younger siblings can provide a suitable analogy.
2. *The Picture in the Mind* diagram (Figure 9) of a square dance is another good analogy for halogen atom reactivity.
3. The use of an analogy of striving for perfection (complete energy level or stable octet) as the reason for the high "desire" of halogens for one more electron can be quite useful.

Pictures in the Mind

Thief: The chlorine atom attracts an electron from the bromide ion to complete its electronic octet (as the chloride ion) and, in so doing, leaves bromine one electron short. It is analogous to a thief at a square dance who completes his square at the expense of someone else.

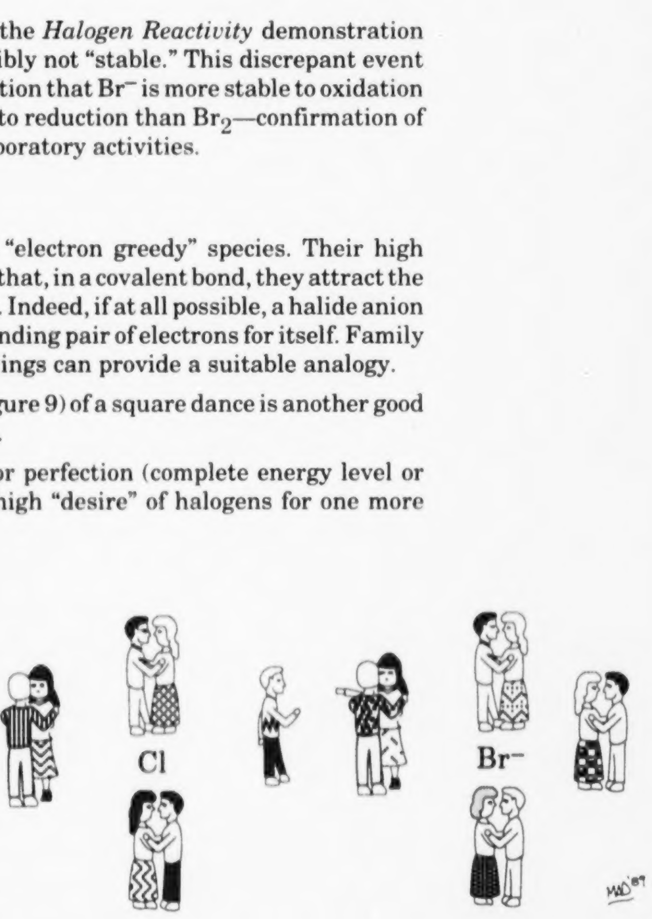


Figure 9. Square dancers representing electrons in Cl^- and Br^-.

Other Activities

1. **Home halogen hunt**. This event can take many forms. Ask students to hunt at home (or at work) for places where halogens are used. This can be accomplished by reading labels or by following a list of possible uses compiled from a source such as an encyclopedia. You can process a wide variety of student responses as a class discussion. Point out that, in almost all cases, the reason for halogen use is its high reactivity or high stability depending upon which form is present.
2. **Pervasiveness of human-introduced halogens in the environment**. There are altogether too many examples of PCBs, insecticides, herbicides, plastics, and chlorofluorocarbons present in the environment. It is useful to note that the very reason these products are used is the same as the reason they plague the environment—their high stability in certain forms. A good background source is *Environmental Chemistry* by Lucy Pryde or *Chemistry in Perspective* by Mohrig and Child.
3. **Chlorofluorocarbons and the ozone layer**. This is another contemporary case of persistence that lends itself to a good discussion—not only of the chemistry involved, but also of the possibility that environmental impact considerations should be placed ahead of personal convenience and comfort.
4. **Use of fluoride as a preventive measure for tooth decay**. Many communities have placed this question on the ballot with passion evident on both sides of the issue. Here is a vehicle to inform your community regarding this issue. An excellent background source is a fluoridation article in the August 1, 1988 issue of *Chemical and Engineering News*.

TIPS FOR THE TEACHER

Language of Chemistry

Bromine nomenclature

Bromide	Br^-	Hydrobromic acid	$HBr(aq)$
Bromine	Br_2	Hypobromous acid	$HOBr$
Hypobromite	BrO^-	Bromous acid	$HBrO_2$
Bromite	BrO_2^-	Bromic acid	$HBrO_3$
Bromate	BrO_3^-	Perbromic acid	$HBrO_4$
Perbromate	BrO_4^-	Bromine dioxide	BrO_2
Dibromine oxide	Br_2O		

Chlorine nomenclature

Chloride	Cl^-	Hydrochloric acid	$HCl(aq)$*
Chlorine	Cl_2	Hypochlorous acid	$HOCl$
Hypochlorite	ClO^-	Chlorous acid	$HClO_2$
Chlorite	ClO_2^-	Chloric acid	$HClO_3$
Chlorate	ClO_3^-	Perchloric acid	$HClO_4$
Perchlorate	ClO_4^-	Chlorine dioxide	ClO_2
Dichlorine oxide	Cl_2O		

*Gaseous HCl should be called hydrogen chloride.

See overhead transparency master for structure of oxoanions.

Fluorine nomenclature

(Given its high electronegativity, it is limited to –1 and 0 oxidation states)

Fluoride	F^-	Hydrofluoric acid	$HF(aq)$*
Fluorine	F_2		
Oxygen difluoride	OF_2		

*Gaseous HF should be called hydrogen fluoride

Iodine nomenclature

Iodide	I^-	Hydroiodic acid	HI (aq)
Iodine	I_2	Hypoiodous acid	HIO
Hypoiodite	IO^-	Iodous acid	HIO_2
Iodite	IO_2^-	Iodic acid	HIO_3
Iodate	IO_3^-	Periodic acid	HIO_4
Periodate	IO_4^-	Iodine dioxide	IO_2
Diiodine oxide	I_2O		

Fluorocarbon – A $(CF_2)_n$ polynuclear species

Freon – Organic chlorofluorocarbon compound; *i.e.*, a hydrocarbon with chloro and fluoro substitution in place of some or all hydrogens of the parent hydrocarbon

General Tips

1. *Emphasize to students that bleach and ammonia should never be mixed.* Chloramine, the result of reaction between chlorine or hypochlorites with ammonia, is very toxic. This caution is also important regarding household cleaning materials, where again, products containing ammonia or ammonia derivatives should not be mixed with products containing chlorine or chlorine derivatives.
2. The mix of laboratory activities and demonstrations you select in teaching about halogens depends on fume hood facilities available to you and your students. *Safety considerations are vitally important with halogens.*
3. Check regarding any respiratory problems or color blindness of students before undertaking this module. Students with respiratory problems should be allowed to observe the laboratory activities, but should probably not be allowed to come close enough to conduct the activities themselves. Color-blind students should be told the observed colors in cases where a color change is undetectable by them.

Pattern Recognition

1. **Periodic Table and oxidizing ability**. This module allows students to develop relationships between the oxidizing ability of elements and their Periodic Table positions. From *Laboratory Activity 2*, students learn that $Cl_2 > Br_2 > I_2$ in terms of oxidizing ability. The extension to F_2 as the strongest is straightforward. Extension to the left on the Periodic Table is hinted at in questions provided with the laboratory activity—you can expand upon this, if you wish. Sulfur (relative to chlorine) provides a simple example beyond oxygen.
2. **Periodic Table and halide acid strength**. Although the hydrohalic acids HCl, HBr, and HI are essentially completely ionized in aqueous solution, HF is a weaker acid. The small size of fluorine and hydrogen atoms can be used to justify the greater attraction between the two. This can be extended to the left in the Periodic Table as well—for example, water is a much weaker acid than is hydrogen sulfide.
3. **Periodic Table and atomic and ionic sizes**. As just noted, fluoride is the smallest halide ion and fluorine is the smallest halogen molecule. The sizes of halogens can be related to their physical properties, *e.g.*, electrons on larger halogen molecules are less tightly held by the nuclei and interact with neighboring halogen molecules (London dispersion forces) more strongly. Halogens become less volatile as the group is traversed from top to bottom, from gases (F_2 and Cl_2), to liquid (Br_2), and to solids (I_2 and At_2) at room temperature.

Common Student Misconceptions

1. **"HF is a strong acid."**

   This incorrect notion arises, in part, since hydrofluoric acid is remarkably reactive, particularly with glass (silica):

   $$SiO_2(s) + 6HF(aq) \rightarrow SiF_6^{2-}(aq) + 2H_3O^+(aq)$$

   However, HF is a weak acid in terms of its low ionization in water.

2. **"Chlorine hysteria."**

   Many individuals and some environmental groups have what could be termed "chlorine hysteria"—they seem unable to ascertain the important difference between chlori*ne* and chlori*des*.

3. **"All silver halides are insoluble in water."**

   Actually, silver fluoride, AgF, has very high water solubility (greater than 10 mol/L at room temperature).

4. **"The light in a halogen lamp is caused by a halogen."**

   A halogen lamp is actually a tungsten filament lamp with iodine added to trap tungsten atoms as they vaporize from the filament. The lamp body is intentionally small; this insures the lamp is hot enough to keep the tungsten iodide in the vapor state until it hits the very hot filament. There it decomposes back to tungsten and iodine, allowing the tungsten to return to the filament.

Problem Solving

1. Identification of a laboratory unknown (see *Laboratory Activity 2*)
2. Risk assessment (see *Decision Making*)
3. Solving the environmental pollution problem—this can be handled in a fashion analogous to the fluoridation example described in *Decision Making*.

Decision Making

This module's *Group Activities* includes a section on water fluoridation as a preventive measure to help prevent tooth decay. A useful (although time consuming) event that will help students become more responsible citizens is to stage a public hearing (debate) on a hypothetical ballot question asking voters to decide whether this should be done. Divide the class into two groups, establish hearing procedures, appoint a moderator (yourself?) and challenge each side to get the facts and support their side.

A key to the public hearing is to explore whether the risk of fluoridation is outweighed by its benefits. Students will be forced to decide and then support a position regarding this issue.

This hearing could be held before a larger audience and be videotaped—or whatever else you think will help instill a sense of "reality." You need to encourage, however, sound scientific arguments and respect for alternative beliefs. The opportunity to practice tolerance and understanding of other positions is one of many benefits of this type of activity.

HISTORY: ON THE HUMAN SIDE

1. **Fluorine** (L. *fluo*, flow) was not prepared as an element until 1886, even though the fluorine-containing mineral fluorspar or fluorite was described in 1529 by Georg Bauer, the German physician and mineralogist better known as Agricola. It appears likely that crude hydrofluoric acid was first prepared in the early 18th century by an unknown English glassworker and used to etch glass. Subsequently, in 1771, Swedish chemist Carl Wilhelm Scheele obtained impure hydrofluoric acid—over a hundred years before French chemist Henri Moissan isolated the element in 1886. The delay was largely due to the reactivity and toxicity of fluorine. After the nearly anhydrous hydrofluoric acid was prepared in 1809, French scientist André-Marie Ampère suggested (1811) that it was a compound of hydrogen with an unknown element, analogous to chlorine, for which he suggested the name fluorine. Fluorspar was then recognized to be calcium fluoride.

   Fluorine's toxicity caused serious health problems for several chemists. Sir Humphry Davy tried to prepare the element by electrolytic decomposition of various fluorides, but succeeded only in ruining his health. French chemist Edmond Frémy, as well as George and Thomas Knox of the Irish Academy, Gay-Lussac, and Thénard all suffered loss of health due to their efforts to make fluorine. At least two chemists—Paulin Louget and Jerome Nickles—died as a direct result of attempts to isolate fluorine. Even Moissan, who finally prepared the gas by electrolysis of anhydrous hydrofluoric acid containing KHF_2 as an electrolyte, had earlier completed many unsuccessful experiments, resulting in damage to his health. He received the Nobel prize in 1906, when he was 54, but died the following year. Prior to World War II, fluorine remained a laboratory curiosity. The use of uranium(VI) fluoride in the separation of uranium isotopes and development of organic fluorine compounds and polymers has made fluorine an important and much more familiar element.

2. **Chlorine** (Gr. *chlorous*, greenish-yellow) was discovered in 1772 by Scheele, who thought it was an oxygen-containing substance. By 1810, Humphry Davy had completed a careful search for the oxygen, but, failing to find any, changed its name from oxymuriatic acid (muriatic acid is HCl and chlorine is an oxidation product of HCl) to chlorine, since he was convinced this was an element. He had some difficulty convincing the French of this, but his views eventually prevailed. Chlorine has been directly or indirectly involved in human history for centuries. At one time salt (NaCl) was more valuable than gold—wars were fought over the control of its sources. Chlorine gas was used as a weapon in World War I, but by contrast, in 1988 it became a federally required water disinfectant in all U.S. public drinking water supplies. Chlorine and other halogen-containing hydrocarbons show a similar apparent dichotomy in their use in a wide variety of consumer, agricultural, and industrial products, while also being banned because of environmental and health concerns. Even so, halogen-containing polymeric hydrocarbon derivatives continue to ease our everyday lifestyle.

3. **Bromine** (Gr. *bromos*, stench) This element's discovery is credited to French chemist Antoine Jérome Balard, who, in 1826, noted that bromine could be liberated from a solution of residues remaining after sodium chloride had been removed from sea water by bubbling chlorine through the solution. He deduced that this was a new element similar to chlorine because the distillation of these residues (containing $MgBr_2$) with manganese dioxide and sulfuric acid also produces bromine and is analogous to a known procedure for producing chlorine. German chemist Justus von Liebig had actually isolated bromine prior to its discovery by Balard, but he interpreted its properties (between those of chlorine and iodine) as indicative of iodine chloride.

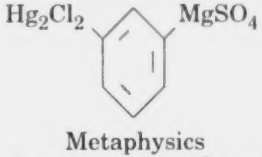
4. **Iodine** (Gr. *iodes*, violet) The discovery of iodine is credited to French chemist Bernard Courtois. In 1811, from the ashes of burnt seaweed, he observed a violet vapor that attacked his copper vessels. He called the condensed black crystalline product "substance X." In 1813, Davy, who was passing through Paris, recognized substance X as an element analogous to chlorine and suggested the name iodine. Historically, iodine has been prepared by a number of methods and sources ranging from extraction from sea kelp and sea animals to various methods of I^- oxidation and IO_3^- reduction.
5. **Astatine** First prepared in 1940 by bombardment of bismuth with alpha particles.

HUMOR: ON THE FUN SIDE

1. Yes, another "groaner":

HAIL - O GEN ! HOW GOES THE OXIDATION WARS ?
MAD 89

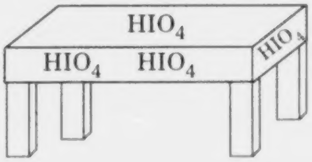
2. HIOAg = Hi O Silver—the Lone Ranger rides again!
3. Hg_2Cl_2 $MgSO_4$



(Both salts have been used as cathartics or physics; 1,3 substitution is called *meta* substitution.)

Metaphysics

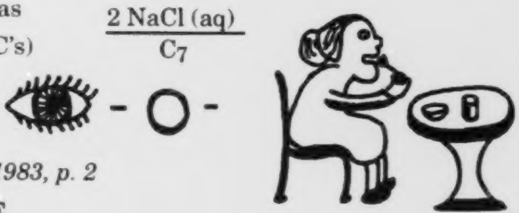
4. A restaurant is where *iodine*.
5. When I go home I walk on the *fluorine* my house.
6. Chlorous Line: $HClO_2$—$HClO_2$—$HClO_2$—$HClO_2$—$HClO_2$
7. Periodic Table:



8. Sailing, sailing, over the 7 seas
(Saline – saline – over the 7 C's)

$$\frac{2\ \mathrm{NaCl\,(aq)}}{C_7}$$

9. **WHAT'S THIS?**



Answer: Iodine (I dine!)
CHEM 13 NEWS, February 1983, p. 2

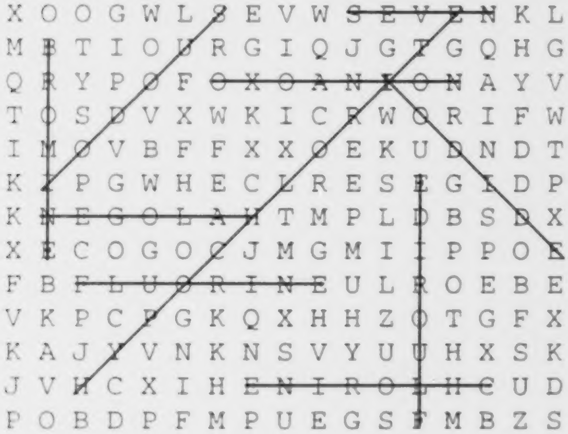
10. **ON SNIFFING CHLORINE**

Donald asked his teacher if,
The jar of chlorine he could sniff:
Teacher queried, as he rose,
"How do we waft a gas to nose?"
Donny grinned and waved a hand;
In the jar his nose he slammed,
Donny crumpled in a fall;
The teacher ran for ethanol.

First aid was rendered on the spot
But Don said he felt "not so hot."
And since he surely was not well
They sent him to the hospital.
From his bed he soon arose
And was putting on his clothes
When nursie caught him in the act;
She hid his clothes without much tact.

Now in bed, no pen or ink,
He had the time to think and think.
He understood the reason why
The teacher used to cry, and try
To get his students to take care
And mix a gas with lots of air,
And breathe in tiny little sniffs;
Not gulp down gas in great big whiffs.
(CHEM 13 NEWS, February 1979, p. 2)

11. Word Search (see *Appendix* for master copy)



X O O G W L S E V W S E V E N K L
M B T I O U R G I Q J G T G Q H G
Q R Y P O F O X O A N K O N A Y V
T O S D V X W K I C R W O R I F W
I M O V B F F X X O E K U D N D T
K I P G W H E C L R E S E G I D P
K N E G O L A H T M P L D B S D X
X E C O G O C J M G M I I P P O E
F B F L U O R I N E U L R O E B E
V K P C P G K Q X H H Z O T G F X
K A J Y V N K N S V Y U U H X S K
J V H C X I H E N I R O L H C U D
P O B D P F M P U E G S F M B Z S

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Name of the anion ClO^-.
2. Most electonegative halogen.
3. Halide used to prevent tooth decay.
4. Halogen that is a yellow-green gas.
5. Largest halide anion.
6. General name of XO^- ion.
7. Number of electrons in outer energy level (any halogen).
8. Salt former.
9. Halogen that is a deep red liquid.
10. Name of the acid HIO_2.

Answers: 1. HYPOCHLORITE 2. FLUORINE 3. FLUORIDE 4. CHLORINE 5. IODIDE 6. OXOANION 7. SEVEN 8. HALOGEN 9. BROMINE 10. IODOUS

12. Halogens Crossword Puzzle (see *Appendix*)
13. See relevant cartoons at end of module.

MEDIA

1. The *World of Chemistry* (high school version) videotape "Number 8: Chemical Bonds" includes a demonstration of a nitrogen triiodide explosion using a feather to detonate the solid and the spectacular synthesis of table salt when sodium metal is added to chlorine gas. WINGS for Learning/SUNBURST, 101 Castleton Street, Pleasantville, NY 10570; (800) 321-7511; (914) 747-3310; (914) 747-4109 (FAX).

2. A number of activities on the *Doing Chemistry* videodiscs (distributed by the Education Division, American Chemical Society, 1155-16th Street, N.W., Washington, DC 20036) relate to this halogen module. Macintosh computer materials provided with the videodiscs aid in use of the videodiscs, although the 630-page *Teacher's Guide* eliminates the *need* for a Macintosh. Here are relevant parts (location on the videodisc is given in parenthesis).

DEMO C02 (C02720)	*Preparation and Sublimation of Iodine*
EXPT E28 (E33508)	*MicroScale Iodine Clock Reaction*
EXPT F43 (F21505)	*A Kinetics Study of the Ferric Ion / Iodide Ion Reaction*

The latter requires a colorimeter connected to a recorder or computer. A simple setup is provided as an Apple II add-on:

DMEX F02 (F00195) *Building and Testing a Blocktronic I Colorimeter*

3. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   a. *KC? Discoverer with Knowledgeable Counselor,* by Daniel Cabrol, John W. Moore and Robert C. Rittenhouse. Special Issue 2, for IBM PS/2, PC compatible computers.

   b. *KC? Discoverer: Exploring the Properties of the Chemical Elements,* by Aw Feng and John W. Moore. Vol. I B, No. 1, for IBM PS/2, PC compatible computers.

c. *KC? Discoverer?,* by Michael Liebl, Vol. IV A, No. 2, for all Apple II computers.

d. *The Periodic Table Stack,* by Michael Farris. Vol. I C, No. 1, for the Apple Macintosh.

4.Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, Wl 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

For the Apple II computer: AP 207, AP 605.

5. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, Wl 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

a. "Changes of State in Bromine," a chapter on *The World of Chemistry: Selected Demonstrations and Animations*: Disc II (double sided, 60 min.), Special Issue 4.

b. "Bromination of Alkanes," "Addition Reactions of Alkenes," and "Acetylene – Preparation and Reactions," three chapters on the videodisc *Demonstrations in Organic Chemistry* (double sided, 60 min.), Special Issue 6.

c. *The Periodic Table Videodisc* (single side, 30 min.). Special Issue 1. The videodisc includes frames of the following:

Element	Element Shown	Reactions	Uses
Fluorine	Not shown	Not shown	6411-22
Chlorine	14228	14234-16819	36510-15
Bromine	35171	35187-36284 (base only)	36732-49
Iodine	45067	45079-46088 (base only)	36924-29

6.*The Science Series* of Media Guild Video (England) provides excellent demonstrations of the reactions of Na through S with F_2 in the videotape segment "Elements Organized." These are demonstrations that cannot be done in a normal classroom.

7. A section of the CHEM Study film *Chemical Families* deals with halogens and is recommended, as is the CHEM Study film *Bromine: Element from the Sea.* New versions of the CHEM Study films have recently been released as videotapes. Available from Ward's Natural Science Establishment, P.O. Box 92912, Rochester, NY 14692-9012. Toll free: 800-962-2660.

8. Coronet Films 1966 production *The Halogens* has been recommended as appropriate. Coronet/NTI Film and Video, 108 Wilmot Road, Deerfield, IL 60015; (800) 621-2131; (708) 940-3640 (FAX).

EQUIPMENT AND INSTRUMENTATION

The primary equipment requirement for this module is availability of fume hoods and adequate ventilation within the room where activities are to be conducted. The venting of both the hoods and the room should be to the outside and *not* to another room or rooms within the building.

Links/Connections

WITHIN CHEMISTRY

1. See Related Concepts and Skills for the most direct links.
2. Chemistry of halogens is very important in organic chemistry—many haloorganics can be synthesized easily and have been found to have very useful properties.
3. Halogen chemistry has importance in inorganic chemistry—inorganic halides provide starting materials for other inorganic species and organometallics. By contrast, some halogen-containing substances, such as sulfur hexafluoride (SF_6), are very inert dielectrics (and find use commercially because of their inertness).

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

1. **Agriculture**. Organic halogen compounds are very important in agriculture. Some important uses include polychlorinated organic compounds as insecticides (such as DDT); fluoro and chloro aromatic heterocyclic compounds and urea derivatives as herbicides; and chlorinated and organic compounds as solvents. Chlorinated inorganic compounds include chlorine bleach as a disinfectant, and salt blocks for animals in hot weather. For more details, see "Organic Halogen Compounds" and "Halogens" entries in the *Encyclopedia Britannica* or some other modern encyclopedia.
2. **Environmental science**. The escape of large numbers of chlorofluorocarbons (Freons) into the upper atmosphere where they can react photochemically with ozone is thought to be causing a depletion of the ozone layer, especially near the South Pole. This problem involves an ironic twist—Freons are chemically inert and have been used to replace toxic materials in many applications such as refrigeration, where ammonia (which is very toxic when released in large quantities) was the common refrigerant prior to synthesis of Freons. Environmental science is also concerned with potential side effects, both in humans and nature, of some agriculturally important haloorganics and with the effects that chlorination of impure water supplies may have on formation of toxic haloorganics in water.
3. **Hygiene**. Halogen chemistry contributes to personal hygiene (*e.g.*, dentifrices containing tin(II) fluoride, sodium fluoride, or a fluorophosphate; antiperspirants and deodorants containing aluminum chlorhydrate; and other preparations containing sodium chloride). In the public health arena, water purification with chlorine is considered so important that all public water supplies in the United States must be treated with chlorine. Chlorine is also used to treat sewage sludge. Although an excellent antibacterial, pHisohex is only available by prescription; doctors use it for surgical scrubbing in certain cases only.
4. **Photography**. Silver halides (particularly AgBr, though AgCl and AgI have been used as well) are the basis of the photographic industry. For more details, see the *Photochemistry* module.
5. **Polymer science**. Polyvinyl chloride, PVC = $(CH_2–CHCl)_n$, is useful in a variety of common applications, including electrical insulation, rainwear fabrics and upholstery fabrics. Poly(tetrafluoroethylene) [Teflon = $(CF_2–CF_2)_n$] and poly(chlorotrifluoroethylene) [Kel–F = $(CClF–CF_2)_n$] have excellent electrical resistance, thermal stability, heat conductivity, and low intermolecular forces (low friction) and are used for thermal coatings, bearings, lubricants (in low molecular weight forms), heat transfer insulators, *etc*. Viton-fluorinated copolymers are related derivatives that are very thermally stable elastomers.

TO THE CONTEMPORARY WORLD

Community

Field Trips

1. Water plant to see chlorination of water process
2. Sewage disposal plant to see chlorination of sewage sludge and reclaimed water
3. Manufacturing facilities as appropriate

Societal

1. See *Discussion Activities.*
2. Air conditioning has become widespread as a result of Freon use. If Freon use were to be discontinued immediately as a result of ozone layer depletion, finding a substitute that does not have even more serious problems would be a real concern.
3. Deodorants and air quality; see *Discussion Activities.*

References

Module developed by Ronald D. Archer, William G. Cumming, and Abraham M. Rennert, the New England team.

Epstein, I. (1987, March 30). Patterns in time and space. *Chemical and Engineering News*, *65*(13), 24-36.

A number of these oscillating reactions contain halogen compounds, but details may be beyond typical high school students. On the other hand, exceptionally able students can find these challenging.

Fortman, J. J. (1993, September). A simpler tomato juice demonstration of halogen addition to double bonds. *Chem 13 News*, p. 30.

Franz, H. W., and Malm, E. (1968). *Fundamental experiments for college chemistry* (2nd Ed.). San Francisco, CA: Freeman.

Greenwood, N. N., and Earnshaw, A. (1984). *Chemistry of the elements.* Oxford: Pergamon.

Hileman, B. (1988, August 1). Fluoridation of water. *Chemical and Engineering News*, *66*(31), 26-42.

Excellent information on the use of fluoride as a preventive measure for tooth decay.

Kolb, D. (Ed.). (1988). *Journal of Chemical Education*, *65*(11), 1004-1005.

This short note contains two overhead projector oscillating-reaction demonstrations appropriate for this module.

Mohrig, J. R., and Child, W. C., Jr. (1987). *Chemistry in perspective.* Newton, MA: Allyn & Bacon.

Good background source for this module.

The New Encyclopaedia Britannica. (1990). Chicago, IL: Encyclopedia Britannica.

See Organic halogen compounds, Halogens, Photography (Technology of), in this or other modern encyclopedia for additional information concerning halogens.

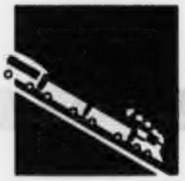
Pryde, L. (1973). *Environmental chemistry*. Menlo Park, CA: Benjamin/Cummings.

Good background source for this module.

Shakhashiri, B. Z. (1983). *Chemical demonstrations: A handbook for teachers of chemistry, Volume 1.* Madison, WI: University of Wisconsin Press.

The following are relevant to this module: Demonstration 1.25: Reaction of Sodium and Chlorine; Demonstration 1.26: Reaction of Antimony and Chlorine; Demonstration 1.28: Reaction of Aluminum and Bromine; Demonstration 1.29: Reaction of White Phosphorus and Chlorine; and Demonstration 1.30: Reaction of Red Phosphorus and Bromine.

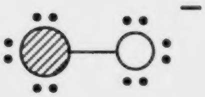
Topics in Chemistry: Ozone–Chlorofluorocarbons and the Hole in the Ozone Layer., available from ICE–Institute for Chemical Education, Department of Chemistry, Universit of Wisconsin-Madison, 1101University Avenue, Madison, WI 53706-1396: (608) 262-3033 (voice) or (608) 262-0381 (FAX).



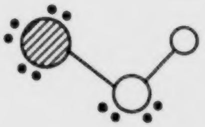
Appendix

- **Transparency Masters**
  1. Oxoanions and Acids of Chlorine
  2. The Halogens
  3. Word Search
  4. Halogens Crossword Puzzle
- **Humor**

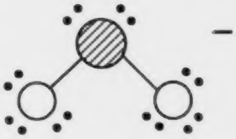
Oxoanions and Acids of Chlorine



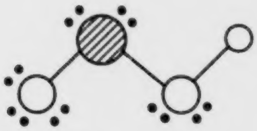
Hypochlorite: ClO^-



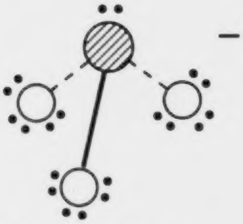
Hypochlorous acid: HOCl



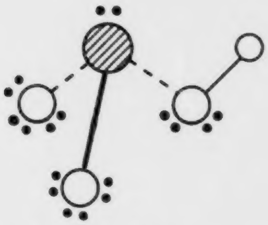
Chlorite: ClO_2^-



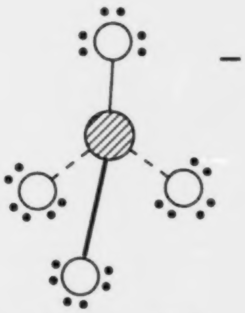
Chlorous acid: $HClO_2$



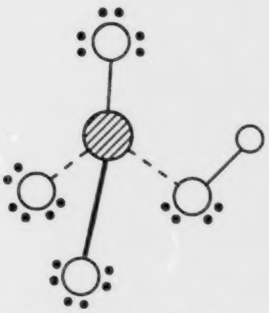
Chlorate: ClO_3^-



Chloric acid: $HClO_3$



Perchlorate: ClO_4^-



Perchloric acid: $HClO_4$

▨ = Cl ○ = O ○ = H

The Halogens*

Element		At. Mass	Normal Form at STP		b.p., °C
Fluorine	F	19.0	F_2	pale-yellow gas	–187.0
Chlorine	Cl	35.5	Cl_2	greenish-yellow gas	–34.5
Bromine	Br	79.9	Br_2	red-brown liquid	58.0
Iodine	I	126.9	I_2	black solid (mp: 113 °C)	184.0

* Astatine, a less familiar element, is not included.

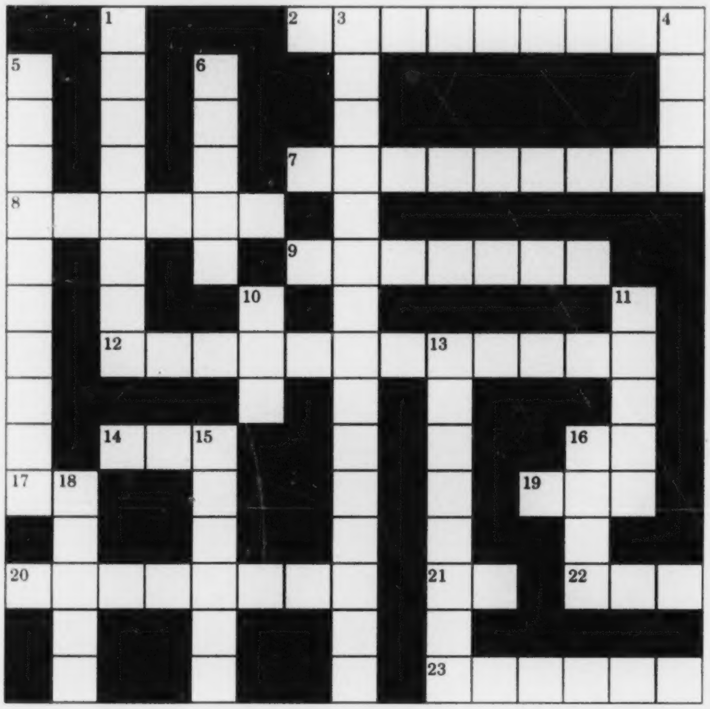
Word Search

X	O	O	G	W	L	S	E	V	W	S	E	V	E	N	K	L
M	B	T	I	O	U	R	G	I	Q	J	G	T	G	Q	H	G
Q	R	Y	P	O	F	O	X	O	A	N	I	O	N	A	Y	V
T	O	S	D	V	X	W	K	I	C	R	W	O	R	I	F	W
I	M	O	V	B	F	F	X	X	O	E	K	U	D	N	D	T
K	I	P	G	W	H	E	C	L	R	E	S	E	G	I	D	P
K	N	E	G	O	L	A	H	T	M	P	L	D	B	S	D	X
X	E	C	O	G	O	C	J	M	G	M	I	I	P	P	O	E
F	B	F	L	U	O	R	I	N	E	U	L	R	O	E	B	E
V	K	P	C	P	G	K	Q	X	H	H	Z	O	T	G	F	X
K	A	J	Y	V	N	K	N	S	V	Y	U	U	H	X	S	K
J	V	H	C	X	I	H	E	N	I	R	O	L	H	C	U	D
P	O	B	D	P	F	M	P	U	E	G	S	F	M	B	Z	S

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Name of the anion ClO^-.
2. Most electonegative halogen.
3. Halide used to prevent tooth decay.
4. Halogen that is a yellow-green gas.
5. Largest halide anion.
6. General name of XO^- ion.
7. Number of electrons in outer energy level (any halogen).
8. Salt former.
9. Halogen that is a deep red liquid.
10. Name of the acid HIO_2.

Halogens Crossword Puzzle



Across

2. Salts containing ClO_3^-.
7. HIO_3 (two words)
8. Element contained in CFC's.
9. BrO_3^-
12. $NaIO_3$ (two words)
14. Oxidation number (in Stock notation) for chlorine in chlorites.
16. Element No. 2 (Symbol)
17. Element No. 98 (Symbol)
19. Hydrocyanic acid (Formula)
20. ________ acid, HIO_4
21. Element No. 30 (Symbol)
22. Oxidation number for bromine in 3-Down.
23. Type of covalent bond where four electrons are shared.

Down

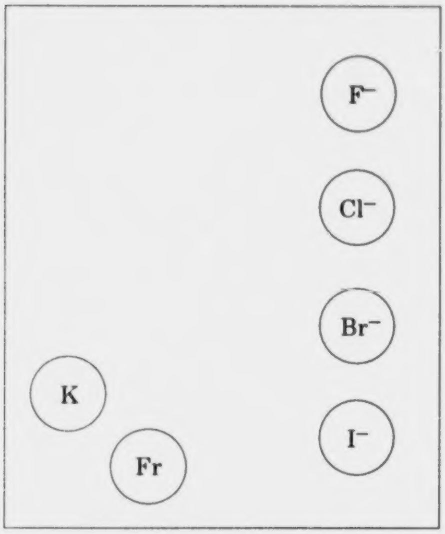
1. ________ acid, $HClO_2$
3. HBrO (two words)
4. Silicon dioxide
5. ________ acid, $HClO_4$
6. Root for Element No. 9.
10. Hypoiodous acid (Formula)
11. Oxidation number of chlorine in 5-Down.
13. Chlorine must be ________ to form 5-Down from chloric acid.
15. ________ acid, HIO_2
16. Hypochlorous acid (Formula)
18. An organic chlorofluorocarbon compound.

Across

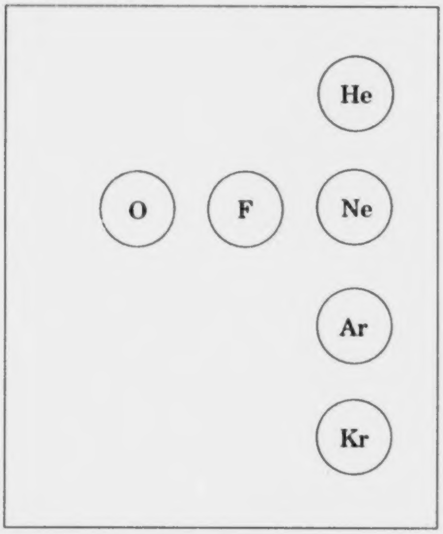
2 CHLORATES
7 IODIC ACID
8 CARBON
9 BROMATE
12 SODIUM IODATE
14 III
16 He
17 Cf
19 HCN
20 PERIODIC
21 Zn
22 ONE
23 DOUBLE

Down

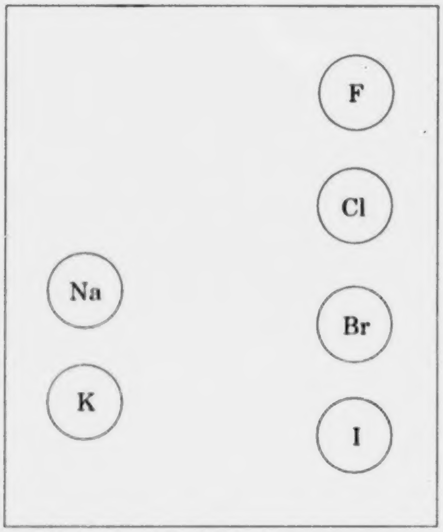
1 CHLOROUS
3 HYPOBROMOUS ACID
4 SAND
5 PERCHLORIC
8 FLUOR
10 HIO
11 SEVEN
13 OXIDIZED
15 IODOUS
16 HClO
18 FREON



"It's disgusting Kay, Flo's family gets such a charge from picking up stray electrons."

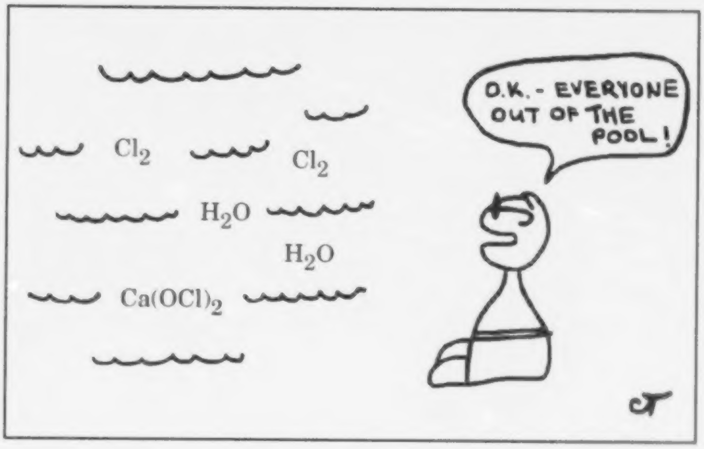


"Flo, I don't know how you stand living in such a conservative neighborhood."

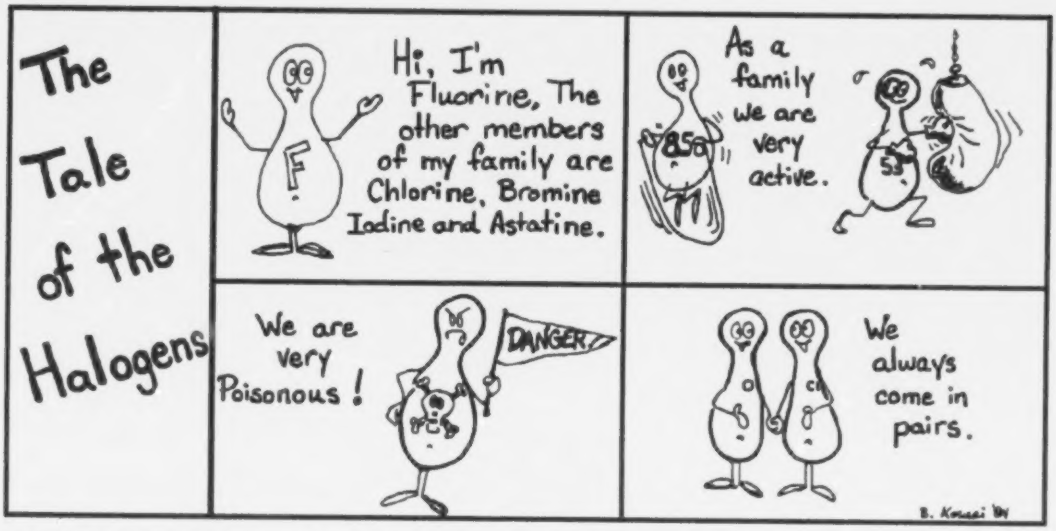


"Take, Take, Take, that's all those halogens ever do."

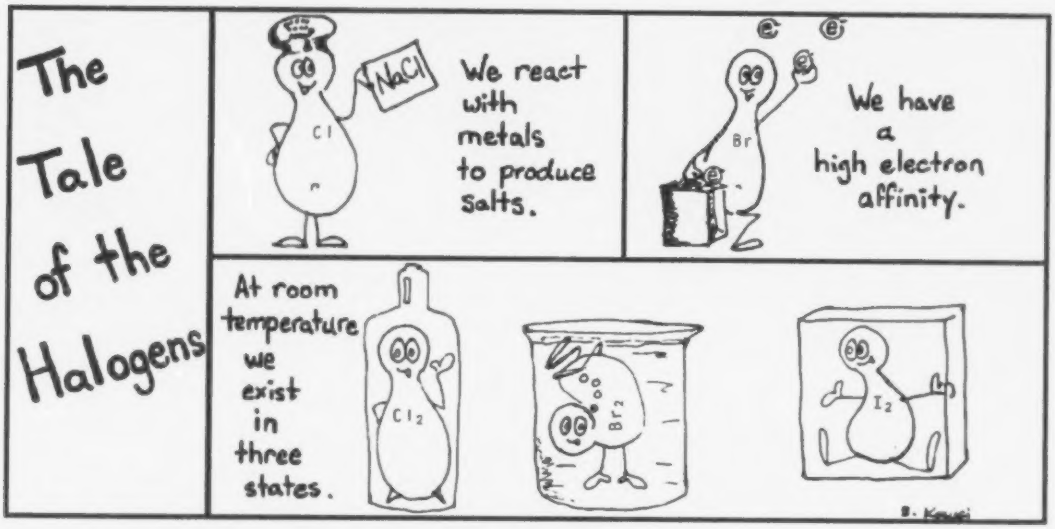
© John Ihde, Wausau West High School, Wausau, WI 54401. Reprinted with permission.


O.K. - EVERYONE OUT OF THE POOL!
Cl_2
Cl_2
H_2O
H_2O
$Ca(OCl)_2$
CT

CHEM 13 NEWS, September 1983, p. 4. Reprinted with permission.


The Tale of the Halogens
Hi, I'm Fluorine, The other members of my family are Chlorine, Bromine Iodine and Astatine.
F
As a family we are very active.
85
53
We are very Poisonous!
DANGER
We always come in pairs.
Cl
Cl

CHEM 13 NEWS, January 1985, p. 14. Reprinted with permission.


The Tale of the Halogens
Cl
NaCl
We react with metals to produce salts.
e
e
e
Br
We have a high electron affinity.
At room temperature we exist in three states.
Cl_2
Br_2
I_2

CHEM 13 NEWS, March 1985, p. 11. Reprinted with permission.

A SourceBook Module

Version 2.0 1994

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INDUSTRIAL INORGANIC CHEMISTRY

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Topic Overview

CONTENT IN A NUTSHELL

Industrial chemistry includes the application of chemistry to the manufacture of chemical substances. The processes used in industry frequently differ significantly from those used in the laboratory. Often the conditions that exist on a small scale when reactions are carried out in beakers and flasks are not the same as are encountered when a reaction is attempted in large vats. Today most chemicals are manufactured in continuous processes. Frequently this requires that a different reaction be used because the laboratory preparation cannot be adapted to the requirements of industry.

Industrial chemicals are produced in large quantities. If a substance is manufactured in only small quantities, it is referred to as a **fine chemical**. The Appendix contains a list of the top chemicals in terms of quantity manufactured. (This information is published annually by the American Chemical Society in *Chemical and Engineering News*.) This list contains many substances familiar to the beginning chemistry student. Sulfuric acid heads the list of inorganic chemicals. It is widely used in the manufacture of other chemicals. Ethylene is always near the top, if not at the top, of the list of organic chemicals. It is used extensively in the plastics industry as well as in the manufacture of a wide variety of organic chemicals. Ammonia, nitric acid, and phosphoric acid are important in the fertilizer industry. (Sulfuric acid is also important in the fertilizer industry, but it has many other industrial applications as well.)

Because of the importance of fertilizers to world food production and the utilization of several of the top chemicals in that industry, the activities and demonstrations in this module focus on the fertilizer industry. Even if there is no fertilizer industry nearby, students can relate to this because of the importance of food in their lives. (Most teenagers love to eat!) Many areas have nearby agricultural regions where the application of fertilizers can be observed and knowledgeable individuals can be found to discuss this important topic with students.

Metallurgy is another important facet of the application of industrial chemistry. The extraction of metals from their ores involves a number of processes. Some steps in the separation procedure are physical processes while others involve chemical reactions. Because of the emphasis in many areas on recycling of aluminum and the energy savings accompanying aluminum recycling, aluminum is a particularly good model for study. The importance of iron (steel) to the economy and its widespread use make iron production another interesting metallurgical process.

Quality control (or quality assurance) is an important aspect of a chemical manufacturing plant. Many chemists and chemical engineers are employed in this support group within a chemical manufacturing plant, testing industrial products to insure that they meet the specifications desired. Raw materials are tested to see that the starting materials are of the proper quality to give the desired product. Finished products are tested before distribution to insure that they meet standards claimed by the manufacturer.

Industrial chemistry is the point at which chemistry, chemical engineering, business, and many other areas begin to overlap. In this module, there is ample opportunity for students to utilize many other disciplines. The history of industrial chemistry provides insight into the lives of many chemists and those who were not chemists but were drawn to chemistry because of economic or other reasons. For example, Leopold Godowsky and Leopold Mannes were professional musicians who had an interest in photography. In high school they began to experiment with color photography. They continued their collaboration for many years, finally developing the process for making Kodachrome™ film, which remains one of the best color processes.

The impact of economic or political conditions on chemical manufacturing also provides a fascinating study. For example, the manufacture of ammonia in the U.S. increased rapidly at the end of World War I due to the urgent war-time need for nitrates. The first full-size plant for the production of HNO_3 from NH_3 was built in Muscle Shoals, Alabama in 1917. The ammonia industry also expanded during the 1940s and 1950s due to World War II and the Korean Conflict.

Social issues related to industrial chemistry include problems related to waste disposal from large chemical plants as well as disposal of chemicals by individuals (*e.g.*, pesticides). The responsibility of the government to regulate manufacturing practices (*e.g.*, air quality in the vicinity of chemical plants) provides an opportunity for students to discuss the impact of governmental regulations on industry and *vice versa*.

PLACE IN THE CURRICULUM

This is an enrichment topic. Since the background material comes from many modules, different sections can be used throughout the course. In order to use all the material, this module should be placed late in the course. The activities in this module illustrate practical applications of stoichiometry, qualitative analysis, and pH measurements.

CENTRAL CONCEPTS

1. Industrial production and use of fertilizers
2. Metallurgy
3. Scaling up
4. Contribution of the chemical industry to agriculture
5. Impact of the chemical industry on the economy and world trade

RELATED CONCEPTS

1. Mole
2. Balancing equations
3. Stoichiometry
4. Redox reactions
5. Kinetics
7. Electrochemistry
8. Thermochemistry
9. Acids and bases
10. Percent composition

RELATED SKILLS

1. Qualitative analysis skills
2. pH measurement
3. Mass and volume measurements
4. Problem solving strategies (dimensional analysis, *etc.*)
5. Algebraic manipulations
6. Observation

PERFORMANCE OBJECTIVES

After completing their study of industrial inorganic chemistry, students should be able to:

1. describe several industrial processes.
2. discuss the process of scaling up reactions for industrial use.
3. express an appreciation for the role of chemistry and chemical manufacturing processes in food production and other areas of their everyday life.
4. discuss the relationship of the chemical industry to the economy.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Physical and Chemical Examination of Soil

Introduction

The successful American society and our comfortable lifestyle is largely a result of the ability of our nation to feed its population. Without maintaining American soils, this food supply will dwindle. This activity is designed to examine only a few of the characteristics that farmers and soil scientists must understand and control.

Purpose

To illustrate the relevance of chemistry in the agricultural industry by examining the oxygen level, humus content, and pH of soil.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Do not touch hot crucibles. They look just like cool ones.
3. Follow proper procedures for lighting burners.
4. Follow usual safety procedures for handling equipment and chemicals.
5. Dispose of waste as directed by your teacher.

Part A. Oxygen Level in Soil

Procedure

1. Place about 200 g bright red clay type soil in a flask or jar that can be closed tightly.
2. Add about 50 g sucrose (table sugar) and mix thoroughly with the soil.
3. Add enough water to cover the soil to a depth of about 3-5 cm.
4. Close the container tightly. It should be kept at room temperature or warmer for about 2 weeks. During this time, the color of the soil should begin to change. Carefully note the color of the soil at the beginning and end of the activity.
5. Thoroughly wash your hands before leaving the laboratory.

Implications and Applications

1. To what is the red color of the soil primarily due?
2. What did the sugar have to do with the processes taking place over the two-week period?
3. Why is a proper level of oxygen necessary for plants?
4. Based on your observations in this activity, describe a technique you could use to compare relative amounts of iron content of various samples of soil.

Part B. Humus Content in Soil

Your teacher will supply you with either a local soil sample or a commercial potting material.

Procedure

1. Weigh a clean, dry crucible and cover.
2. Fill the crucible about half full with soil and reweigh the crucible and cover. Note the color of the soil. Dry the crucible and contents overnight in a drying oven at about 60 °C.
3. Record the mass of the soil and crucible after drying. (The soil is referred to as "dry soil" throughout *Part B* of the activity.) Note the color of the soil.
4. Place the crucible in a clay triangle on a ring stand. Heat it with a hot flame for 30 min. Stir the soil with a glass stirring rod occasionally while heating. Be sure to use a hot flame.
5. Allow the crucible and soil to cool. Weigh the crucible, cover, and soil.
6. Record the color of the soil and general appearance before drying, after drying, and after heating strongly for 30 min.
7. Repeat the procedure using a commercial potting soil or peat moss.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

Data Chart

A. Mass of empty crucible and cover. __________

B. Mass of crucible, cover, and soil before drying overnight. __________

C. Mass of crucible, cover, and soil after drying overnight. __________

D. Mass of dry soil after overnight heating at 60°C. (C-A) __________

E. Mass of crucible, cover, and soil after strongly heating for 30 min. __________

F. Mass of soil after heating strongly for 30 min. (E-A) __________

G. Mass of humus lost during 30 min heating. (D-F) __________

Using the mass of the "dry soil" before it was strongly heated (D) and the mass loss as a result of strongly heating the "dry soil" (G) calculate the percent by mass humus in the original sample of soil (B-A). (This calculation assumes that the mass loss during the 30 min of intense heating is due to the burning of the humus.)

Implications and Applications

1. Why is it desirable to dry the soil overnight before the intense heating process?
2. During the 30 min of heating strongly, why does only the humus volatilize?
3. How do the results for the commercial potting material compare with the other soil sample? Why are the results different?
4. Why is humus important for plant growth?
5. Composting organic wastes is strongly encouraged. Explain what composting is and how it would be useful in efforts to protect the environment and improve the soil.

Extension

Use the mass of the soil before and after drying overnight at 60 °C (C-B) to determine the percent water by mass in the original sample.

Part C. Soil pH

Part C1. Measuring the pH

1. Allow several soil samples to air-dry for two or three days.
2. Weigh 10 g of a sample of air-dried soil and mix it thoroughly with 10 mL of distilled water. Stir and let it sit for 15-20 min.
3. Stir the mixture again. Measure the pH using a pH meter, pH test papers, or pH indicator solutions provided by your teacher. Record your pH measurement.
4. Follow Steps 2 and 3 for each soil sample.
5. Thoroughly wash your hands before leaving the laboratory.

Data Analysis, Observations, and Concept Development

Note the source of the soil for each sample. Record the pH. Observe the color and odor, if any, for each sample. Compare the pH, color, and odor for the different samples.

Part C2. Changing the pH

1. Weigh 50 g air-dried soil and place it in a beaker or flask.
2. You will be assigned a substance to be tested for pH. Carefully add 0.5 g of the assigned substance to the soil sample and mix thoroughly.
3. Slowly add just enough water to moisten the soil (about 20-30 mL).
4. Repeat Steps 2 and 3 for each material to be tested for its effect on soil pH.
5. Cover the samples and allow to stand for one to two weeks, keeping the sample moist *but not saturated* throughout this time.
6. After this period of time, weigh 10 g of each treated soil and add 10 mL of water. Stir and allow to stand for 15-20 min.
7. Stir again and measure and record the pH.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Prepare a data chart showing the substance(s) you used and the resulting pH measured. How much did each substance change the pH from the pH measured before the substance was added (as measured in *Part C1*)?

Implications and Applications

1. If the pH changed, how is the direction of change related to the chemical properties of the substance added?
2. In a reference source, find the most desirable pH for optimal growth of several types of plants.
   a. Do all these plants have the same optimum soil pH?
   b. What type of plant would be best suited to the soil sample you tested?
   c. For a plant that would not grow as well in your soil sample, what could you use to treat the soil to provide more appropriate growing conditions?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Physical and Chemical Examination of Soil

Major Chemical Concept

This activity helps show the relevance of mass percent calculations, pH determinations, oxidation-reduction reactions, and Brønsted-Lowry acid-base reactions. This activity could be substituted for more traditional laboratory activities to illustrate the application of chemical principles such as pH or oxidation-reduction.

Level

All levels

Expected Student Background

Part A requires an understanding of simple oxidation-reduction reactions (see *Oxidation-Reduction* module). For *Part B*, students should be able to calculate percent by mass. *Part C* requires an understanding of the concept of pH and the use of pH paper, pH indicators or a pH meter to measure pH (see *Acids and Bases* module). Familiarity with standard laboratory procedures is assumed.

Time

Preparation of the soil sample in *Part A* requires about 15 min. The samples should be observed every few days over the following two weeks. Observations require only a few minutes since the only data to be collected is color change.

Part B may be done in one class period (50 min). *NOTE: Pre-drying overnight is required before this activity.*

If soil samples have been air-dried for two to three days, the sample can be prepared (Step 1 of *Part C1*) prior to beginning *Part B* and the pH measurement in *Part C1* can be made while students are waiting for complete combustion of the soil sample in *Part B*. There may also be sufficient time during the intense heating of the soil sample in *Part B* to prepare the samples for *Part C2*. Again, the observations during the one to two-week incubation period do not require much time. The pH measurements require only a few minutes.

Safety

Read the *Safety Considerations* in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

Balance
12 Burners
12 Graduated cylinders, 10-100-mL
12 Flasks (or some type of container that can be closed)
12 Crucibles
12 Crucible tongs
12 Ring stand set ups with clay triangles
12 Wire gauze
pH meter (optional)
Drying oven

Consumables

Soil samples *[NOTE: If red clay soil is not available in your area, it can be simulated by thoroughly mixing a few grams of finely powdered Fe_2O_3 with local soil.]*
Commercial potting soil, 600-900 g
Distilled water
pH paper, indicator solutions or pH meter
Sucrose (table sugar), 600 g
Substances to affect pH—5 g each of one or more of these:
Calcium carbonate, $CaCO_3$
Calcium oxide, CaO
Calcium sulfate, $CaSO_4$
Commercial "lime"
Ammonium chloride, NH_4Cl
Ammonium sulfate, $(NH_4)_2SO_4$

Advance Preparation

1. All equipment and supplies should be available to students. This saves much time in set up. Equipment should be checked to insure proper working condition.
2. For *Part B*, soil samples should be predried overnight at about 60 °C.
3. For *Part C* students will need 100-500 g or more of each soil sample, depending on the moisture content of the soil and how many substances you will be testing for their effect on pH of the soil. If you use a pH meter, standardize the meter before the laboratory period.

Pre-Laboratory Discussion

1. If this is used as an activity replacing more traditional activities, demonstrate the technique for measuring pH using the method you have chosen for this measurement. If you use a pH meter, it is important to explain that meters are standardized and should not be arbitrarily adjusted during the activity.
2. Safety should be stressed especially with emphasis on hot and cold porcelain looking the same.

Part A

Proper levels of oxygen in the soil are needed for plant growth and microorganism activity. Many chemical reactions in the soil are carried out aerobically by microorganisms. One of the most important of these is the decomposition of plant and animal material by bacteria and fungi. The release and conversion of nitrogen contained in organic substances is dependent on a well aerated soil. The level of oxygen in the soil can be examined by observing its color. Oxygen rich soils generally have bright-colored red subsoils. Soils that have gray subsoils are usually deficient in oxygen.

The oxidation state of iron is responsible for the color of the soil. A red, oxygen-rich soil contains iron(III) oxide, Fe_2O_3. A gray subsoil contains iron largely as iron(II) oxide. In the case of the gray subsoil, the iron has been reduced from iron(III) to iron(II). This reaction occurs because the microorganisms could not obtain oxygen from the air in the soil, usually because the soil is too wet. Thus the microorganisms use the oxygen bonded to the iron in the iron(III) oxide converting the iron(III) to iron(II). Sugar is added in this activity to supply the energy needed by these microorganisms.

This activity provides a real-life illustration of oxidation-reduction.

Part B

Plant and animal material returned to the soil after the death of the organism forms the humus content of soils. Humus is a source of nutrients that can replenish what is removed by growing plants. Many of these nutrients (*e.g.*, carbon and nitrogen) are cycled through our ecosystems and are a subject of much study (see *Biogeochemical Cycles* module). These cycles could be presented during the pre-laboratory discussion.

Part C

Many factors affect pH of soils such as fertilizers, type of soil, rainfall, season, type of crop grown the previous season or the type of plants (trees, shrubs, *etc.*) found in the area. Because optimum growth conditions for different plants occurs at different pH values, soil samples may be too acidic or too basic depending on the types of plants one wishes to grow. (For example, most vegetables prefer a pH between 6 and 8.) A good gardener will know the optimum pH for the plants and will adjust the soil pH accordingly. "Lime" is commonly used to raise soil pH. Anhydrous or aqueous ammonia will also raise soil pH. However, continued use of ammonia (and fertilizers containing ammonium ion) leads to an increase in soil acidity by microbial oxidation of NH_4^+ to NO_3^-. Crop fertilization can increase soil acidity because many fertilizers contain ions (*e.g.*, NH_4^+) that tend to lower the pH of the soil. Also rainfall leaches neutral and basic substances more readily than acids, increasing surface soil acidity. These factors increase the tendency of cultivated soils to be acidic unless treated with lime. If soil is too basic, pine needles or almost any type of tree leaves can be added to lower the pH.

Brønsted-Lowry bases increase soil pH by reacting with excess H^+ ions in acidic soils. Calcium carbonate, calcium oxide, and commercial "lime" are examples of substances that can neutralize acidic soils.

$$H^+(aq) + CaCO_3(s) \rightarrow HCO_3^-(aq) + Ca^{2+}(aq)$$

$$2H^+(aq) + CaO(s) \rightarrow H_2O(l) + Ca^{2+}(aq)$$

If equal masses are used, CaO will cause a larger pH increase than will $CaCO_3$. Commercial "lime" is frequently a mixture of substances such as $CaCO_3$ and $MgCO_3$. Since $CaSO_4$ is the salt of a strong acid and strong base, it will not neutralize acid and thus will not affect the soil's pH. Brønsted-Lowry acids decrease soil pH by reacting with excess OH^- ions in basic soils. Ammonium salts (*e.g.*, NH_4NO_3) can neutralize basic soils.

$$OH^-(aq) + NH_4^+(aq) \rightarrow H_2O(l) + NH_3(g)$$

Teacher-Student Interaction

1. The degree of supervision required will depend upon whether this activity is used as an alternate to other activities to illustrate the concepts of percent by mass and pH or as an enrichment activity. During long periods of heating crucibles, discuss observations with students.
2. Discuss with students how materials in *Part C2* are responsible for affecting pH.
3. Do not be concerned that variations in results are obtained when the same soil samples are used since no attempt has been made to provide uniform soil samples. Differences may also be greater if a visual method (pH paper or indicator) is used to measure pH.

Anticipated Student Results

Don't expect student data to agree closely for these activities. Interest is generated, however, by having students analyze local soil samples. Use this opportunity to discuss reasons for differences in student results.

Part A

Within two weeks, the bright red soil should begin to turn gray as the microorganisms use the combined oxygen, reducing iron(III) to iron(II).

Part B

It is not possible to predict the mass percent humus you will obtain due to the variations among soil types and to nonuniformity of samples. It is better to collect class data and compare. The commercial potting soil should be more consistent.

Part C

Results will vary with the soil samples. For *Part C2*, the following pH values are typical results for the various compounds used to affect the soil pH. These are not absolute values, just possible results. Allow for differences among soil samples and student interpretation of colors if indicators are used.

Always keep a sample of the original untreated soil to use as a control for comparison.

Calcium carbonate	6.8
Calcium oxide	7.0
Calcium sulfate	4.5
Commercial lime	6.0

Answers to Implications and Applications

Part A

1. The red color of the soil is primarily due to presence of iron(III) compounds.
2. The sugar was an energy source for the microorganisms during the activity.
3. The proper level of oxygen is necessary because plant roots and other tissues must carry on respiration, which requires oxygen. (Other answers are acceptable.)
4. Student answers will vary. One answer could be to compare relative amounts of iron content of various samples of soil by establishing a color scale like pH indicator scales.

Part B

1. Drying the soil overnight before the intense heating process is necessary so that the humus will burn easily and completely (see also answer to *Question 1* in *Assessing Laboratory Learning*).
2. During the 30 min of heating strongly, only the humus volatilizes because organic matter will oxidize at lower temperatures. The oxidation products are CO_2 and H_2O, which are volatile at the temperatures used. Most inorganic compounds are not volatile at the temperatures reached in the activity and will not be converted to volatile compounds under the conditions of the activity. For example, silicon dioxide, a component of soils, is already fully oxidized.
3. Typically, commercial potting soils will have higher humus amounts because humus is added to provide the nutrients and the mulching effect to aid in aeration.
4. Humus is important for plant growth because it is a source of needed nutrients.
5. Student answers will vary. Composting involves returning waste plant (and sometimes animal) materials to the soil. Compost provides nutrients, principally carbon and nitrogen, to the soil.

Part C

1. The direction of change related to the acid/base nature of the substance added. Substances that are Brønsted-Lowry bases raise pH. Substances that are Brønsted-Lowry acids lower pH.
2. a. There is variation in optimum soil pH for different plants.
   b. Answer will depend on soil pH.
   c. Answer will depend on soil pH.

Post-Laboratory Discussion

1. Collect class data for all activity parts and discuss similar and dissimilar findings. Identify the source of all soil samples to facilitate this discussion. Is there a correlation between the source of the soil sample and the color (oxygen content), percent humus, and/or pH?
2. Ask if students noticed large pieces of material in soil samples that might cause variations in experimental data if not removed. In commercial analysis, careful drying and sieving of samples is used to provide sample uniformity. Although results show much more variation without this treatment, most high school laboratories are not equipped to prepare samples in this manner. Also, the time required can be considerable.
3. Questions should be posed about the chemical reasons behind the pH values obtained in *Part C2*. Discuss Brønsted-Lowry acid-base reactions for species such as $CaCO_3$, $CaSO_4$, and CaO (plus any other substances used) and their effect on pH.
4. Ask questions about the role of chemistry in agriculture and discuss the effect on the food industry and the economy.

Extensions

1. Invite someone from the county agricultural extension service to talk with your classes about fertilizers, *etc.*
2. Discuss fertilizers and their components.
3. Include the major industrial processes that are involved in making the raw materials from which fertilizers are made such as the Haber process, the Ostwald process, the contact process, *etc.* in a class discussion.
4. Grow some plants in different pH soils and watch the effects of pH.
5. Contact a nursery and arrange for a tour of their facilities with an expected emphasis on soil chemistry.

Assessing Laboratory Learning

Because results will vary, discussion of data is the most effective way of assessing this laboratory activity. The following questions could be used as a basis for the discussion.

1. If a sample is not dried overnight at 60°C before combustion, what would be the effect on the percent humus? Explain. *[Percent humus would be greater because the mass loss would include loss of water as well as loss of organic matter due to combustion.]*
2. Ammonium nitrate (NH_4NO_3) is used as a fertilizer. How does adding NH_4NO_3 affect soil pH? *[Decrease pH]*

3. Which will be more effective in raising soil pH, 1.0 g $CaCO_3$, 1.0 g $MgCO_3$, or 0.50 g CaO? (Assume all reactions go to completion.)

$$H^+(aq) + CaCO_3(s) \rightarrow HCO_3^-(aq) + Ca^{2+}(aq)$$

$$H^+(aq) + MgCO_3(s) \rightarrow HCO_3^-(aq) + Mg^{2+}(aq)$$

$$2H^+(aq) + CaO(s) \rightarrow H_2O(aq) + Ca^{2+}(aq)$$

[CaO will be most effective. 1.0 g $MgCO_3$ will neutralize 0.012 g H^+. 1.0 g $CaCO_3$ will neutralize 0.010 g H^+. 0.50 g CaO will neutralize 0.018 g H^+.]

References: See texts by Jacobs *et al.*, 1971; Kleiss, 1986; and Tocci, 1987 in *References* section of this module.

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: The Solvay Process

Purpose

To illustrate reactions in the Solvay Process, and to produce sodium carbonate by an industrial process.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Gloves for handling dry ice.
3. Thoroughly wash your hands before leaving the laboratory.

Procedure

Part I. Preparation of $NaHCO_3$

1. Obtain a 250-mL gas collection bottle and stopper, 25 X 300-mm test-tube with a stopper assembly, and a length of rubber tubing (see Figure 1).
2. Measure 60 mL 3 M NH_3 in a graduated cylinder and pour into a 250-mL Erlenmeyer flask. Weigh out 20 g NaCl to 0.1 g and add it to the NH_3 solution. Stopper tightly, and shake the solution for several minutes to saturate it with NaCl. If all the NaCl dissolves, add a bit more. When the solution appears to be saturated, filter out the excess solid, using a long-stemmed funnel and filter paper, letting the clear liquid drain into the test-tube.
3. Assemble the apparatus shown in Figure 1. The long rubber tubing should be connected to the bent tube on the stopper assembly. The short straight tube is fitted with a small valve, called a Bunsen valve, which will vent CO_2 if the pressure becomes excessive. A Bunsen valve consists of a short length of rubber tubing containing a short lengthwise slit. The valve lets gas out, but not in.

   Fill the gas collection bottle about half full with crushed solid CO_2 (dry ice). Wrap the bottle with a towel or several paper towels for insulation, and put it into a 600-mL beaker. Insert the stopper firmly in the gas collection bottle.

   If your apparatus is tight, you will observe bubbles of CO_2 in the NH_3-NaCl solution; they should be produced at a vigorous rate, and as they bubble up through the solution they will react with NH_3 and become somewhat smaller. As the reaction goes on, the concentration of HCO_3^- ions will gradually increase. While the reaction is proceeding, begin *Part II* of the experiment. However, check the stoppers occasionally to make sure they haven't popped out.

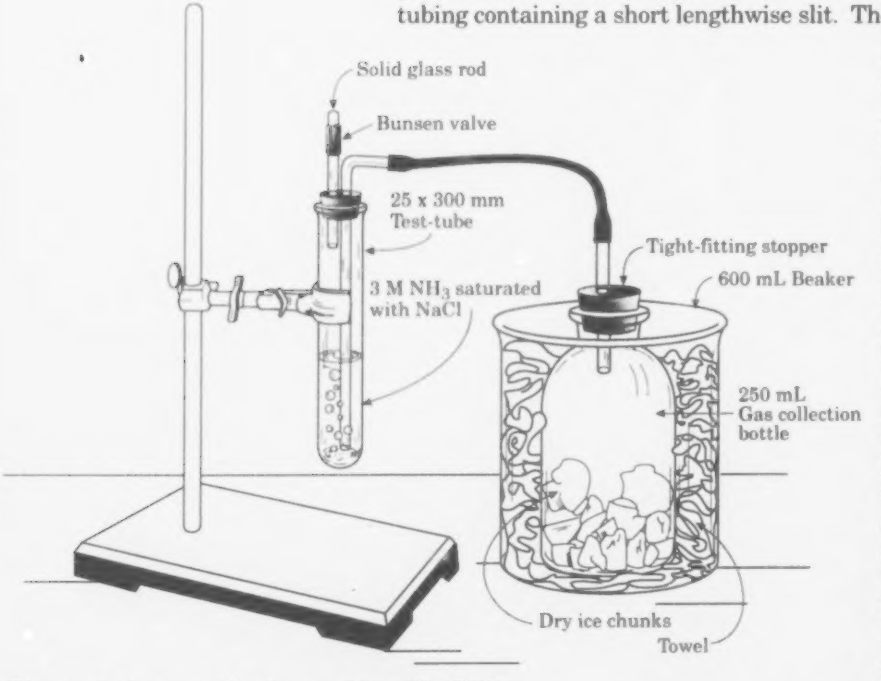


Figure 1. Apparatus for making $NaHCO_3$.

Finally, after about 30 min of bubbling, you should observe a slight cloudiness in the solution as small crystals of $NaHCO_3$ start to form. Continue the bubbling for 30 min more, during which time an appreciable amount of $NaHCO_3$ should form. During the last 15 min cool the large test-tube in an ice bath, which will decrease the solubility of the $NaHCO_3$, and hence, produce more product.

3. Disconnect the stopper from the large test-tube and unclamp it carefully. Cool the tube in an ice bath for several minutes. Filter the $NaHCO_3$, using a Buchner funnel with suction.
4. When all the liquid has been sucked into the suction flask, turn off the suction. Add 3 mL *ice-cold* distilled water to the crystals, wait 10 sec, and then turn on the suction. This should remove most impurities in the $NaHCO_3$. Repeat the procedure with an additional 3 mL of *ice-cold* water.
5. Turn off the suction and pour 5 mL 95% ethanol onto the crystals. Again, wait about 10 seconds and then turn on the suction. Repeat with another 5 mL of ethanol. Then leave the suction on for 2 min to dry the crystals. Turn off the suction, remove the filter paper from the funnel, and with a spatula transfer the crystals to a piece of filter paper weighed to 0.1 g.
6. Weigh the crystals on the paper to 0.1 g. Place a small portion of the product into a small test-tube. Add a few drops of 6 M HCl. The effervescence of CO_2 is indicative of the presence of the HCO_3^- anion in the solid and shows that the solid is not just NaCl.

Part II. Preparation of Na_2CO_3

1. Heat a small evaporating dish to redness. Allow it to cool to room temperature, and weigh it to 0.001 g.
2. Add about one gram of your $NaHCO_3$ product, which should be dry by now, and weigh again to 0.001 g.
3. Heat the evaporating dish and $NaHCO_3$ again to redness, holding it at red heat for about 10 min. Let the sample cool to room temperature and weigh it.
4. Rinse out all equipment and return it to the stockroom.

Data Analysis and Concept Development

Explain why:

1. $NaHCO_3$ is the product obtained from solution made from NaCl, NH_3, and CO_2.
2. It takes about 30 min for the first $NaHCO_3$ to appear.
3. One cannot make Na_2CO_3 directly by reaction of $CaCO_3$ and NaCl.

Data Table

Mass of filter paper ____________________ g

Mass of filter paper + $NaHCO_3$ ____________________ g

Mass of $NaHCO_3$ formed ____________________ g

Mass of evaporating dish ____________________ g

Mass of evaporating dish + $NaHCO_3$ ____________________ g

Mass of evaporating dish + Na_2CO_3 ____________________ g

Mass of $NaHCO_3$ decomposed ____________________ g

Mass of Na_2CO_3 produced ____________________ g

Implications and Applications

Given the reaction shown, answer the following:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2\,(g)$$

1. How many grams of Na_2CO_3 would be produced from 1.00 g $NaHCO_3$?
2. How many grams of Na_2CO_3 were obtained from one gram of $NaHCO_3$ in the sample you decomposed?
3. How would you explain the difference between the results of Questions 1 and 2?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: The Solvay Process

Introduction

Sodium carbonate, Na_2CO_3, ranks in the top twenty industrial chemicals in amount produced in the United States. It is used to make glass, soap, paper, and other substances. Two hundred years ago, before chemistry was a science, sodium carbonate, then called soda ash since it was obtained from wood ashes, was in short supply, and the French government offered a prize for a synthetic method for its manufacture. In 1791 Leblanc developed a process using common salt, limestone, coal, and sulfuric acid. Salt was heated with sulfuric acid and converted to salt cake, Na_2SO_4. Salt cake was heated to about 900 °C with a mixture of coal and limestone, producing a mixture of Na_2CO_3, CaS, and impurities called black ash. The sodium carbonate was leached from the solid with water and recrystallized. It was a rather messy process, but at least it worked! The Leblanc process was used to make Na_2CO_3 during much of the nineteenth century. Following its development in 1865, the Solvay process gradually replaced the Leblanc process and became the source of most of the Na_2CO_3 produced during this century. In 1938, some large deposits of the mineral trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O$, were discovered near Green River, Wyoming and have been extensively mined. They now furnish over half the sodium carbonate needs of this country.

This experiment illustrates some of the reactions used in the Solvay process for making Na_2CO_3. The reactants are table salt (NaCl), ammonia (NH_3), and carbon dioxide (CO_2). A moderately concentrated NH_3 solution is first saturated with NaCl. Carbon dioxide is then bubbled through the resulting solution. It reacts with NH_3 and H_2O to form HCO_3^- and NH_4^+ ions. Among the possible ionic products, sodium hydrogen carbonate, $NaHCO_3$, has by far the lowest solubility in water and crystallizes out (solubility in moles/liter at 0 °C: $NaHCO_3$, 0.82; NH_4Cl, 5.5; NaCl, 6.1; NH_4HCO_3, 1.5). The solubility of $NaHCO_3$ is lower at low temperatures, so the mixture is cooled to about 0 °C to obtain the maximum product yield. The CO_2 for the process is made by heating limestone, $CaCO_3$, with CaO formed as the other product. The NH_3 used is regenerated from the NH_4^+ ions present in the solution, by reaction with CaO. The final products of the first part of the process are $NaHCO_3$ and $CaCl_2$. Sodium carbonate is then made from $NaHCO_3$ by heating the latter to about 300 °C, where it decomposes. The key reactions in the overall Solvay process are summarized below:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{1}$$

$$2NaCl(s) \rightarrow 2Na^+(aq) + 2Cl^-(aq) \tag{2}$$

$$2NH_3(aq) + 2CO_2(g) + 2H_2O(l) \rightarrow 2HCO_3^-(aq) + 2NH_4^+(aq) \tag{3}$$

$$2Na^+(aq) + 2HCO_3^-(aq) \rightarrow 2NaHCO_3(s) \tag{4}$$

$$CaO(s) + 2NH_4^+(aq) \rightarrow 2NH_3(g) + H_2O(l) + Ca^{2+}(aq) \tag{5}$$

$$Ca^{2+}(aq) + 2Cl^-(aq) \rightarrow CaCl_2(s) \tag{6}$$

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g) \tag{7}$$

Net reaction (sum of Reactions 1-7):

$$CaCO_3(s) + 2NaCl(s) \rightarrow Na_2CO_3(s) + CaCl_2(s) \tag{8}$$

Major Chemical Concepts

Solubility, stoichiometry, thermodynamics

Level

General or Basic

Expected Student Background

Students should be able to solve stoichiometry and solubility problems.

Time

Part I 45 to 55 min
Part II 35 to 45 min

Safety

Read the *Safety Considerations* in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

Part I. Preparation of $NaHCO_3$

- 12 Beakers, 600-mL
- 12 Gas collection bottles, 250-mL
- 12 Rubber tubing pieces
- 12 Test-tube clamps
- 12 Ringstands
- 12 Test-tubes, 25- x 300-mm
- 12 Stoppers, Size 2, two-hole
- 12 Stoppers, Size 6, one-hole
- 24 Glass tubing, 10 cm
- 12 Glass bends (A in Figure 1)
- 12 Lab towel
- 12 Bunsen valves (short piece of rubber tubing with 1 cm longitudinal slit with one end fitted with small piece of solid glass rod as a stopper)

Part II. Preparation of Na_2CO_3

- 12 Evaporating dishes
- 12 Burners
- 12 Ringstand, ring, wire gauze set-ups (for heating evaporating dish)

Consumables

- 3 M NH_3 solution, 1 L [dilute 200 mL conc. NH_3 (15 M) to 1 L]
- Sodium chloride, NaCl, 240 g
- Dry Ice, 2 lbs (available from grocery or ice cream stores)

Advance Preparation

Glass elbows must be prepared for the apparatus shown in Figure 1. Follow standard glass forming procedures. Heat the center of the glass tubing, slowly rotating it until it glows a yellow color and becomes flexible. Slowly bend until a right angle is formed. Fire polish all ends. Make sure that the glass tube extends to near the bottom of the test-tube (32 cm from end to bend).

Assemble the apparatus, including the Bunsen valve, as described in *Part I* of the procedure and shown in Figure 1.

Pre-Laboratory Discussion

Possible pre-laboratory discussion questions are:

1. What is the purpose of the Solvay process? *[To prepare Na_2CO_3]*
2. What raw materials are actually used up in the overall process? *[$CaCO_3$ and NaCl]*
3. What are the final products? *[Na_2CO_3 and $CaCl_2$]*
4. If 20 g of NaCl were dissolved in 60 mL 3 M NH_3, assuming 100% yield according to the Solvay process, how much $NaHCO_3$ would crystallize out of the final solution at 0 °C? Assume that NaCl is the limiting reactant, and that the solubility of $NaHCO_3$ is 0.82 moles per liter. (HINT: Moles NaCl = Moles $NaHCO_3$ produced; find moles $NaHCO_3$ remaining in solution and subtract from moles produced.) *[24.6 g $NaHCO_3$]*
5. In the reaction, $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$:
   a. How many grams of Na_2CO_3 would be produced from 1.000 g $NaHCO_3$? *[0.631 g Na_2CO_3]*
   b. How would the mass of Na_2CO_3 per gram $NaHCO_3$, as observed in your experiment, vary from the theoretical value if:
      (1) The $NaHCO_3$ were wet when it was weighed? *[Lower mass of Na_2CO_3]*
      (2) The $NaHCO_3$ contained NaCl as an impurity? *[Higher mass of Na_2CO_3]*

Teacher-Student Interaction

This activity provides an opportunity for students to perform a synthesis using common industrial substances. As the reaction bubbles, ask students why it takes so long before crystals of $NaHCO_3$ begin to form, and why it is necessary to rinse the crystals with water many times. The concepts of saturation and removal of impurities by differences in solubility can be amplified. In *Part II* students can be asked while heating $NaHCO_3$, why it changes to Na_2CO_3. Driving off water and CO_2 by heating is a common process both in the laboratory and in industry.

Anticipated Student Results

Mass of filter paper	1.1 g
Mass of filter paper + $NaHCO_3$	21.1 g
Mass of $NaHCO_3$ formed	20.0 g
Mass of evaporating dish	52.500 g
Mass of evaporating dish + $NaHCO_3$	72.500 g
Mass of evaporating dish + Na_2CO_3	64.500 g
Mass of $NaHCO_3$ decomposed	20.000 g
Mass of Na_2CO_3 produced	12.000 g

Answers to Data Analysis and Concept Development

1. Of all the compounds ($NaHCO_3$, NH_4Cl, NaCl, NH_4HCO_3) possible to make $NaHCO_3$ has the lowest solubility in water.

2. The concentration of $NaHCO_3$ must exceed 0.82 mol/liter before solid $NaHCO_3$ will begin to appear. It also takes some time for the ammonia solution to cool down. The lower the temperature, the lower the solubility of $NaHCO_3$.
3. We need an indirect method of making Na_2CO_3 because the overall reaction shown is not spontaneous:

$$CaCO_{3\,(s)} + 2NaCl_{\,(s)} \rightarrow Na_2CO_{3\,(s)} + CaCl_{2\,(s)}$$

Answers to Implications and Applications

1. 1.00 g $NaHCO_3$ x

$$\frac{1\text{ mol NaHCO}_3}{84.0\text{ g NaHCO}_3} \times \frac{1\text{ mol Na}_2\text{CO}_3}{2\text{ mol NaHCO}_3} \times \frac{106\text{ g Na}_2\text{CO}_3}{1\text{ mol Na}_2\text{CO}_3} = 0.631\text{ g Na}_2\text{CO}_3$$

2. 12.00g Na_2CO_3 / 20.00g $NaHCO_3$ = 0.600 g Na_2CO_3 per gram of $NaHCO_3$.
3. If the mass of Na_2CO_3 is too low possible errors include that $NaHCO_3$ was not dry when heating began, or that splattering occurred during the heating process. If the mass of Na_2CO_3 is too high possible errors include impurities in $NaHCO_3$ and not heating $NaHCO_3$ long enough to drive off all water and CO_2.

Post-Laboratory Activities

Discussion might center around whether the majority of the class has larger or smaller masses of Na_2CO_3 than expected and what could have been done to increase the yield.

Extension

Some students may want to research how sodium bicarbonate and sodium carbonate are made industrially, what quantities are produced annually, and what are their major industrial uses.

Assessing Laboratory Learning

1. If 5.00 g of NaCl is dissolved in 60.0 mL of 3 M NH_3, how much $NaHCO_3$ will crystallize out of the final solution at 0 °C after CO_2 has been bubbled through. The molar solubility of $NaHCO_3$ is 0.82 mole/liter. *[3.05 g]*
2. If 7.05 g of $NaHCO_3$ is recovered, what is the percent yield of $NaHCO_3$? *[7.05g / 6.83g x 100 = 103%]*
3. Which experimental errors could be responsible for this percent yield:
   a. The temperature of the ammonia solution is above 0 °C?
   b. The $NaHCO_3$ was weighed while it was still wet?
   c. There were impurtities in the $NaHCO_3$?
   d. Some $NaHCO_3$ was lost in the filtration process?

   Answer: [b, c]

References

This activity is adapted from Slowinski, E. J., Wolsey, W. C., and Masterton, W. J. (1984). *Chemical principles in the laboratory (3rd Ed.)*, pp. 85-91. Philadelphia, PA: CBS College Publishing, Saunders College Publishing. Background information is found in *Chemical Technology: An Encyclopedic Treatment*, 1968; *Faith, Keyes, and Clark's Industrial Chemicals*, 1975; and *Kirk-Othmer Encyclopedia of Chemical Technology*, 1978-84 (in *References*).

DEMONSTRATIONS

CAUTION: Use appropriate safety guidelines in performing demonstrations.

Demonstration 1: Reaction of Metals with Acid and Base

Purpose

To illustrate the reactions of metals with acid and base.

Materials

6 Test-tubes
6 M Hydrochloric acid, HCl, 100 mL (50 mL 12 M HCl diluted to 100 mL)
25% Sodium hydroxide, NaOH (dissolve 25 g NaOH in 75 g water)
Aluminum (in small pieces, aluminum foil can be used)
Iron filings (or small pieces of iron)
Copper (copper wire or copper tubing can be used)

Safety

Use care in handling the acid and base solutions. Be careful that the mouth of the test-tube is directed away from all people to avoid injury if bumping of the solution occurs during heating.

Procedure

Add 6 M HCl to half-fill three test-tubes. Add 25% NaOH to half-fill the remaining three test-tubes. Add a few iron filings to a tube containing acid and observe. If the reaction is too slow, the tube can be heated gently. *[Iron dissolves as is evidenced by coloration of the acid and formation of bubbles of hydrogen gas.]* Then add a few iron filings to a tube containing the base and observe. When no reaction is observed, the tube can be heated gently. *[No reaction should occur. Heating should have no effect.]* Repeat for copper and aluminum. *[Aluminum and iron should dissolve in acid with evolution of hydrogen gas. Only aluminum will dissolve in base. You may have to heat to observe the reaction, depending on the size of aluminum pieces.]*

Remarks

This demonstration illustrates the amphoteric nature of aluminum. It can be used to explain why aluminum is not a good container to use for highly basic substances. Drano™ contains a mixture of NaOH and aluminum, which react in the drain to generate large amounts of heat and hydrogen gas, causing the "gurgling" action that breaks up clogs in drains. The NaOH is also effective in reacting with fats to "make soap" if greasy foods comprise the mixture clogging the drain. Since many fertilizers contain acidic substances, metal containers should not be used to store fertilizers. Also it is important to wash buckets (galvanized pails are zinc coated) if they are used to transport fertilizer. Although copper will not react with acids, copper alloys (*e.g.*, brass and bronze) contain metals (brass: copper and zinc; bronze: copper and tin and/or other metals such as lead, zinc, aluminum) that do react with acid.

Demonstration 2: Brown Bottle Reaction

Purpose

This demonstration illustrates reactions involved in the synthesis of nitric acid (Ostwald Process).

Materials

Gas generating apparatus (side-arm flask with stopper or Erlenmeyer flask and one-hole stopper fitted with glass tube, rubber tubing, pneumatic trough or plastic tray—see diagram)
Bottle or flask (for collecting NO) with stopper, 200-300 m-L

Copper wire, 1-2 g is probably sufficient (or penny minted before 1982)
Nitric acid, HNO_3, concentrated
Litmus paper, red and blue
Glass plate, 3" x 3"

Safety

Oxides of nitrogen are toxic. This demonstration should be done in a hood. Be careful not to spill HNO_3 on your skin. Concentrated nitric acid can cause severe burns. Nitric acid reacts with skin to produce yellow stains.

Procedure

Set up the gas generating apparatus as shown in Figure 2 to collect NO (nitrogen monoxide) over water.

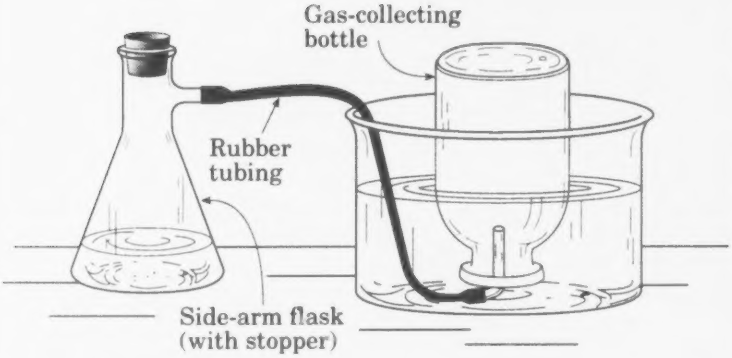


Figure 2. Gas generating apparatus.

Fill the collection bottle with water, cover with glass plate and invert in the pneumatic trough so that the neck of the bottle is below the surface of the water. Remove the glass plate. Place the delivery tube into the collection bottle. Place the copper in the side-arm flask. Add about 5 mL concentrated nitric acid and quickly stopper the flask. The reaction will generate NO. When the bottle is full of NO (colorless gas, but may be slightly colored due to presence of NO_2), remove the bottle and quickly stopper it. [A small amount of water should remain in the bottle. In removing the bottle and stoppering it, enough O_2 will be admitted to oxidize NO to NO_2 (nitrogen dioxide), and the gas in the bottle should turn red-brown due to NO_2.] Shake the bottle and the color disappears as NO_2 dissolves in water. Open the bottle to air briefly and usually enough NO remains to see the color change to red-brown again. Again stopper the bottle and shake until the color disappears. Drop a piece of blue litmus paper into the water in the bottom of the bottle and observe the color change to red (indicating that an acid has been formed). Red litmus should not change color.

Remarks

This demonstration simulates part of the Ostwald Process for formation of nitric acid. Equations for reactions taking place are:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \rightarrow NO(g) + 2HNO_3(aq)$$

Discuss the Ostwald process and the commercial importance of nitric acid in conjunction with this demonstration. *NOTE: NO is generated by the oxidation of NH_3 in the Ostwald process (see* Biogeochemical Cycles *module).*

Demonstration 3: Electrolysis of Aqueous $CuCl_2$

Purpose

Electrolysis is used in the industrial preparation and purification of metals and other substances. This demonstration illustrates the electrolytic preparation of copper by reduction of Cu^{2+} in $CuCl_2(aq)$.

Materials

Beaker
9-V Battery and clip
2 Pencils
2 Wires with alligator clamps on each end (for connecting battery to pencils)
0.1 M Copper(II) chloride, $CuCl_2$ (1.3 g $CuCl_2$ or 1.7 g $CuCl_2 \cdot 2H_2O$ per 100 mL solution)

Safety

Observe the usual safety precautions for handling solutions. Properly dispose of the $CuCl_2$ solution. Since Cl_2 is formed at the anode, the electrolysis should not be allowed to proceed for lengthy time periods unless it is done in a hood. Avoid contact with the closed electrical circuit or with electrical connections before completing the circuit.

Procedure

Set up the electrolysis apparatus as shown in Figure 3. The U-tube can be taped to an inverted cup that serves as a stand. Place the copper chloride solution in the U-tube. Sharpen the pencils (or otherwise expose the graphite) on **both** ends. Using the alligator clamp, attach a wire to one end of each pencil. Immerse the other end of the pencil in the copper chloride solution placing one pencil in each arm of the U-tube. Attach the wires to the electrodes of the battery.

Electrolyze the copper chloride solution until the color begins to fade and Cu(s) begins to form on one electrode (a red copper-colored coating will be visible when the pencil is removed from the solution.)

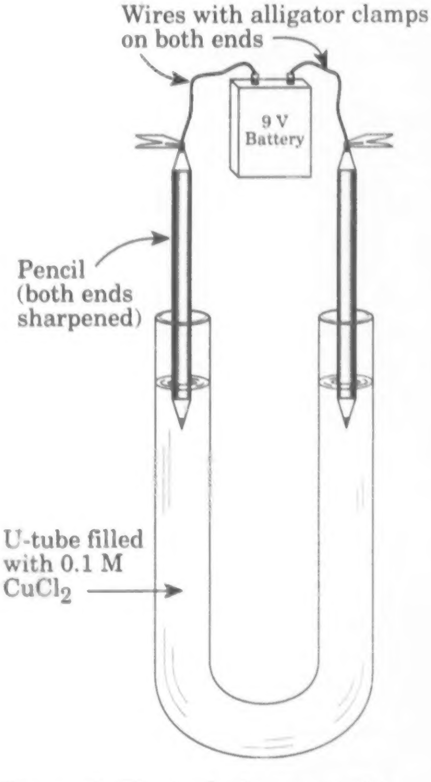

Wires with alligator clamps on both ends
9 V Battery
Pencil (both ends sharpened)
U-tube filled with 0.1 M $CuCl_2$

Figure 3. Electrolysis apparatus.

Remarks

Mechanical pencil "lead" can be used instead of pencils for the electrodes. Attach alligator clamps to one end of the "lead". Immerse the other end in the solution. Failure to react could be due to microfractures in the pencil "lead."

Electrolysis of $CuCl_2$ will produce copper metal at the cathode. The reduction reaction is:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The fading of the blue color is due to the removal of Cu^{2+} ions from the solution as Cu^{2+} is reduced. (The anode reaction produces chlorine. The odor of chlorine can be detected at the anode. This reaction is not pertinent to the purpose of this demonstration, but could be mentioned.)

Although copper is not produced electrolytically, metallurgy of reactive metals such as magnesium and sodium requires electrolysis to obtain the uncombined element. Copper is purified by electrolysis. Impure copper is the anode while pure copper is used for the cathode. During the electrolysis, copper dissolves at the anode and by carefully controlling the electrical potential pure copper is redeposited at the cathode. Other metallic impurities that are less easily oxidized than copper fall to the bottom of the container during electrolysis. This residue is the anode sludge. In copper purification, the anode sludge can contain such precious metals as silver and gold. Sometimes recovery of these metals can actually pay for the electricity required for the purification.

Demonstration 4: Properties of Fertilizers

Purpose

To illustrate conductivity and pH of fertilizers.

Materials

Fertilizer samples (such as 8-8-8, "plant food")
Distilled water
Conductivity apparatus (see *Instrumentation* section)
pH paper or pH meter

Procedure

"Dissolve" a spoonful of fertilizer in 50 mL distilled water. Observe that many commercial fertilizers (such as 8-8-8) are not completely soluble in water. Test for electrolytes by observing conductivity of the solution. Test solution pH using pH paper or a pH meter.

Safety

Observe the usual safety precautions for handling substances.

Remarks

This demonstration leads to discussing differences in fertilizer composition. Fertilizers such as 8-8-8 could be added to water in the same proportions as plant foods or you could simply add "a spoonful" to a small beaker (50 mL) of water. This is a qualitative demonstration and is intended only to illustrate that fertilizers are not neutral and that they are generally conductors because they contain soluble ionic substances. In addition to fertilizers, lime (calcium oxide, CaO) could also be tested.

Extensions

Qualitative tests for several ions could be performed on the fertilizers. Most fertilizers will contain nitrate and phosphate ions. Many also contain calcium and ammonium ions. Plant foods formulated for house plants frequently contain many ions. Read the label to see which ions are present and experiment to see which ones will give "good" tests with your fertilizer sample (see *Inorganic Qualitative Analysis* module or a standard text on qualitative analysis for reagents needed to test for these ions).

Demonstration 5: Soil pH

Part A. Measurement of Soil pH

Purpose

This demonstration illustrates the measurement of soil pH.

Materials

Beaker, 50 mL
Soil sample(s)
Distilled water
pH meter (calibrated with buffers of known pH)

Safety

Use normal safety precautions.

Procedure

Place 10 g of a soil sample in a 50-mL beaker. Add distilled water to form a soft paste. Stir several times during a 30 min period. After 30 min, measure the pH with a calibrated pH meter.

Remarks

This is one method used to measure soil pH. (Usually the soil sample would undergo careful mixing to insure uniformity and would be sieved to remove large particles such as gravel. This could be done if a sieve is available or large particles could be removed upon inspection of the sample.) The pH of the soil is used to determine whether lime needs to be added before growing crops that do not thrive in soils of low pH. If possible, it would be helpful to measure the pH of several soil samples of different types to show how soil pH varies. Students could be asked to bring a sample of soil for measurement. This demonstration could be expanded to a student activity, if desired.

Part B. Reserve *vs.* Active Acidity of Soils

Purpose

Soils contain "free" H^+ ions (active acidity) and H^+ ions that can be released by ion exchange (reserve acidity). This demonstration illustrates a method of measuring both types of acidity.

Materials

Filter paper
2 Funnels
2 Beakers, 50-mL
Soil sample(s)
Distilled water
pH meter (calibrated with buffers of known pH)
0.2 M Potassium nitrate, KNO_3, 20 mL (0.4 g KNO_3 in 20 mL aqueous solution)
Supports for funnels

Safety

Use normal safety precautions.

Procedure

Fold filter paper in fourths and place in funnel. Moisten the filter paper with distilled H_2O and press firmly against the funnel. Add 10 g of soil to each. *Slowly* pour 20 mL of distilled water through one sample and collect the filtrate in a 50-mL beaker. *Slowly* pour 20 mL of 0.2 M KNO_3 through the second sample and collect the filtrate. Measure the pH of both solutions, being careful to rinse the electrode between measurements.

Remarks

Some of the hydrogen ions in the soil are not ionizable when the soil is simply wet with water; however, they can be removed by ion exchange. When the potassium ion replaces these hydrogen ions, they contribute to the acidity of the soil. The pH may be lower in the sample that was extracted with potassium nitrate. (Potassium nitrate solution should be neutral if distilled water is used to prepare the solution. You may want to prepare additional 0.2 M KNO_3 so you can measure the pH of the KNO_3 solution to demonstrate that the effect is not due to the potassium nitrate.)

Reference

See Jacobs *et al.*, 1971, in *References* section.

Other Demonstration Ideas

The Can Ripper

An aluminum can is weakened by treatment with 0.1 M $CuCl_2$ so that it can be torn apart (see directions in the *Group and Discussion Activities* section of the *Oxidation-Reduction* module).

GROUP AND DISCUSSION ACTIVITIES

Key Questions

Key questions for this module will depend upon the emphasis you choose. Suggested questions include:

1. Give the reaction(s) used in some important commercial processes. *[Responses to this question will vary depending upon the processes you discuss. See* Background Notes *for suggestions.]*
2. List some of the chemicals produced in largest quantity worldwide. *[The list of the top chemicals is given in the Appendix. Of those, the ones discussed in the background material for this module include* H_2SO_4, NH_3, HNO_3.*]*
3. What are some important commercial reactions used in the production of fertilizers? *[Responses may vary. Some of the major reactions include:]*

$$\begin{aligned}
N_2(g) + 3H_2(g) &\rightarrow 2NH_3(g) \\
4NH_3(g) + 5O_2(g) &\rightarrow 4NO(g) + 6H_2O(g) \\
2NO(g) + O_2(g) &\rightarrow 2NO_2(g) \\
3NO_2(g) + H_2O(g) &\rightarrow 2HNO_3(aq) + NO(g) \\
HNO_3(l) + NH_3(g) &\rightarrow NH_4NO_3(s) \\
Ca_3(PO_4)_2(s) + 2H_2SO_4(l) + 4H_2O(l) &\rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4 \cdot 2H_2O(s) \\
Ca_3(PO_4)_2(s) + 3H_2SO_4(l) &\rightarrow 2H_3PO_4(s) + 3CaSO_4(s) \\
Ca_3(PO_4)_2(s) + 4H_3PO_4(l) &\rightarrow 3Ca(H_2PO_4)_2(s) \\
2NH_3(g) + H_3PO_4(l) &\rightarrow (NH_4)_2HPO_4(s)
\end{aligned}$$

4. Why does the production of aluminum require the use of electricity while carbon (usually in the form of coke) is used in the production of iron? *[Aluminum is much more easily oxidized than iron; thus, it requires a stronger reducing agent. The only chemical reducing agents that will reduce aluminum (e.g., Mg, Na,* etc.*) also require electricity in their production; thus, it is more practical to produce aluminum directly.]*
5. List some important steps in scaling up from laboratory (bench) scale to industrial scale. *[First the most favorable conditions are sought on the laboratory scale. Then the reaction is tried in a small-sized model of the industrial process. After optimizing conditions on a small scale, the process is tried in a large-sized or developmental unit. The next step is the semi-commercial plant scale and finally the full-scale commercial plant. At any step the reaction may prove to be "unworkable" and require further investigation to find more suitable conditions (perhaps a different catalyst or different temperature or pressure) or even require substituting another reaction to achieve the desired product.]*

Counterintuitive Examples

A bottle of NO containing a small amount of water will develop a red color when the bottle is briefly opened to the air. Shaking the bottle causes the color to disappear. This reaction is involved in the commercial process for nitric acid production (Ostwald process; see *Demonstration 2: Brown Bottle Demonstration*).

Analogies and Metaphors

The human body is sometimes described as a chemical manufacturing plant. Many chemicals are produced from “raw materials” in the body. For example, complex carbohydrates are broken up into simple sugars, which are in turn metabolized to CO_2 and H_2O with the generation of energy. Proteins are decomposed into amino acids and then reassembled to form tissue. (Students may study some of these reactions in biology courses. For an elementary discussion some of these reactions, refer to an introductory college chemistry text designed for allied health students.)

Pictures in the Mind

In the Frasch process three concentric pipes are inserted into a hole drilled down to the sulfur deposit. Superheated water is forced down the outer pipe into the sulfur, causing it to melt. Molten sulfur is then forced up the middle pipe by compressed air.

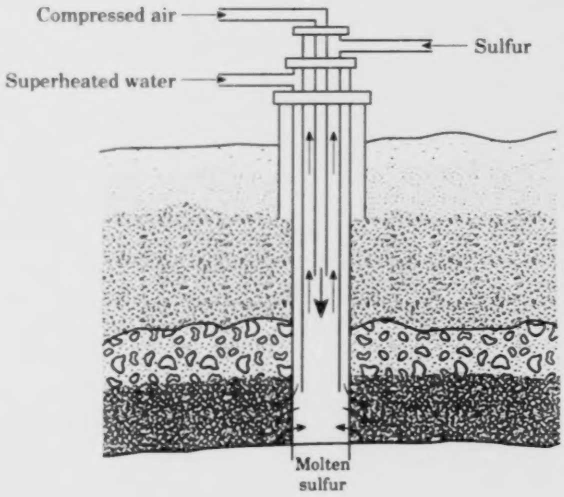


Figure 4. The Frasch process.

TIPS FOR THE TEACHER

Background Notes

Industrial chemistry includes a broad range of manufacturing processes including petroleum refining, preparation of metals from their ores (metallurgy), and production of pharmaceuticals. Industrial chemistry is a broad field, and the discussion in this module is restricted to industrial processes associated with the production of synthetic inorganic fertilizers and the preparation of aluminum from bauxite ore as representative industrial processes. Other commercial processes are discussed in the modules on *Alkali Metals* (Solvay process for sodium carbonate) and *Chemistry in Medicine* (synthesis of aspirin).

The principal ingredients of inorganic (or mineral) fertilizers furnish the elements nitrogen, phosphorus, and potassium in forms that can be utilized by plants. The analysis (or grade) of inorganic fertilizers is expressed as % N, % P (as P_2O_5), and % K (as K_2O). If a fertilizer contains only one of these essential elements, it is referred to as a straight fertilizer. If it contains all three elements, it is said to be a complete fertilizer. Although the nitrogen in mineral fertilizers is generally in the form of ammonium or nitrate salts, anhydrous ammonia, and urea are also used as straight nitrogen fertilizers. The principal substance used as a source of phosphorus is $Ca(H_2PO_4)_2$. Potassium is generally present as potassium chloride (muriate of potash).

Ammonia is prepared by the Haber-Bosch process, developed by Fritz Haber and adapted for industrial-scale use by Carl Bosch in 1913 (see *History*). Nitrogen from the air is reacted with hydrogen at elevated temperatures (500-700 °C) and high pressures (about 200 atm) in the presence of a mixed Fe_3O_4-Mn catalyst.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The hydrogen needed for the reaction is usually produced by steam reforming, the reaction of steam with natural gas (methane, CH_4) or petroleum products such as propane (C_3H_8) using an iron oxide-chromium oxide catalyst.

$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$$

$$CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$$

These processes tie the cost of fertilizer production, and hence the cost of food production, to the cost of petroleum and natural gas (see *History*).

The largest single use for ammonia is direct application of anhydrous ammonia as a fertilizer. There are several advantages of using anhydrous ammonia as a fertilizer, such as the ability to apply it prior to or after planting. Anhydrous ammonia combines with clay and organic matter to resist leaching loss, a significant problem with nitrate fertilizers.

Because anhydrous ammonia requires special equipment to apply, solid fertilizers are desirable. One such fertilizer can be prepared by oxidation of ammonia to nitric acid followed by reaction of the resultant nitric acid with ammonia to form ammonium nitrate. Almost all the nitric acid commercially produced is prepared by the Ostwald process. Ammonia is oxidized in air over a platinum catalyst at 850 °C and atmospheric pressure to form nitrogen monoxide (nitric oxide, NO), which is further oxidized to NO_2 by reaction with oxygen. Reaction of NO_2 with water produces nitric acid and NO, which is recycled to produce more nitric acid.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$3NO_2(g) + H_2O(g) \rightarrow 2HNO_3(aq) + NO(g)$$

The largest use for nitric acid is in the manufacture of ammonium nitrate for fertilizers.

$$HNO_3(l) + NH_3(g) \rightarrow NH_4NO_3(s)$$

The other major use for nitric acid is in making explosives.

Phosphorus fertilizers are generally prepared by the reaction of sulfuric acid with phosphate rock, principally $Ca_3(PO_4)_2$.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(l) + 4H_2O(l) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4{\cdot}2H_2O(s)$$

Although $Ca_3(PO_4)_2$ can be used directly as a phosphate fertilizer, its limited solubility renders it marginally effective. Reaction of phosphate rock with sulfuric acid produces $Ca(H_2PO_4)_2$, which is soluble and hence a more effective phosphorus fertilizer. The mixture of $Ca(H_2PO_4)_2$ and $CaSO_4{\cdot}2H_2O$ formed by the above reaction is known as "superphosphate".

Currently, 85% of the fertilizer phosphate produced in the U.S. is based on phosphoric acid. Rather than producing a mixture of $Ca(H_2PO_4)_2$ and $CaSO_4{\cdot}2H_2O$, additional sulfuric acid is added to produce H_3PO_4.

$$Ca_3(PO_4)_2(s) + 3H_2SO_4(l) \rightarrow 2H_3PO_4(s) + 3CaSO_4(s)$$

The phosphoric acid produced by this method is known as "wet-process" phosphoric acid and is contaminated with impurities from the phosphate rock. Usually these impurities do not significantly affect the use of the acid in fertilizer production. If "wet-process" phosphoric acid (instead of sulfuric acid) is added to phosphate rock, "triple superphosphate" is produced.

$$Ca_3(PO_4)_2(s) + 4H_3PO_4(l) \rightarrow 3Ca(H_2PO_4)_2(s)$$

"Wet process" phosphoric acid is also used to prepare $(NH_4)_2HPO_4$, diammonium hydrogen phosphate or DAP, by direct reaction of ammonia and phosphoric acid.

$$2NH_3(g) + H_3PO_4(l) \rightarrow (NH_4)_2HPO_4(s)$$

In 1977, 64% of the phosphate fertilizer used in the U.S. was diammonium hydrogen phosphate.

Sulfuric acid, required for the production of "wet-process" phosphoric acid and "superphosphate", is the chemical produced in largest quantity world-wide. Until recently, sulfuric acid production was used as a measure of the economic strength of a nation. Because of its extensive use in the production of phosphate fertilizers (2/3 of the annual production is used for this purpose), and because large quantities of phosphate fertilizers are produced in eastern Europe and other countries lacking other industries, sulfuric acid production is no longer an accurate measure of the economy.

In the production of sulfuric acid, sulfur is reacted with oxygen from the air in the presence of a V_2O_5 catalyst at 410-430 °C to form SO_3.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

SO_3 reacts with sulfuric acid to form pyrosulfuric acid, $H_2S_2O_7$. Pyrosulfuric acid is reacted with water to form sulfuric acid.

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

This indirect method of reaction of SO_3 with water is used because the amount of heat generated in the process is extremely large. (Also SO_3 is not very soluble in water.) The two-step process facilitates the dissipation of heat. The large quantity of thermal energy accompanying the reaction may be used to produce steam for the generation of power via turbines. This synthesis for sulfuric acid is known as the Contact process.

Sulfuric acid is used in many industrial processes in addition to fertilizer production. It is used extensively in the manufacture of other substances as well as in the paper industry. Over 70% of the sulfuric acid produced annually is used directly by the producers to make other materials. Because production costs are small compared to shipping costs, most sulfuric acid is produced close to the site of use.

More than 85% of the sulfur consumed worldwide is converted to sulfuric acid. The sulfur required for the Contact process is obtained from two principal sources. Formerly most sulfur was obtained from native sulfur deposits and was mined by the Frasch process. In the Frasch process, three concentric pipes are drilled to the level of the sulfur deposit. Superheated water at 160 °C is forced down the outer pipe. The hot water melts the sulfur. Compressed air is forced down the center pipe. The compressed air mixes with the water-sulfur slurry, aerating the liquid sulfur and causing it to rise to the surface through the middle pipe (see diagram in *Pictures in the Mind*). The sulfur thus obtained is a liquid and is usually shipped as a liquid (rather than solid). In 1980, the output of sulfur by the Frasch process was about 8.1 million tons.

Currently about half of the world's elemental sulfur production is recovered sulfur. Most of the recovered sulfur is obtained from "sour" natural gas and petroleum by the Claus process. "Sour" natural gas contains hydrogen sulfide (or organic sulfides) which on burning produces SO_2, a primary air pollutant. Thus, the Claus process serves two purposes: to reduce pollution that would result from combustion of the untreated gas and to produce sulfur. The principal reactions in the Claus process are:

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$$

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

These reactions are carried out at atmospheric pressure in the presence of a bauxite (aluminum oxide) catalyst.

In addition to nitrogen and phosphorus, the third major element in fertilizers is potassium. About 90% of potassium fertilizer is potassium chloride, KCl. Prior to 1965, New Mexico furnished most of the KCl used in fertilizers. Today KCl is mined extensively in Canada. Several methods of purification are used to concentrate the potassium chloride and remove undesirable impurities, principally NaCl. One of these is the "thermal method". At 100 °C, KCl is more soluble than NaCl in a saturated KCl/NaCl solution while at 30 °C, NaCl is more soluble. (At 100 °C, the mass percent solubility of KCl in saturated KCl/NaCl is 21.65% while the solubility of NaCl is 16.90%. At 30 °C, the mass percent solubility of KCl in saturated KCl/NaCl is 11.70% while the solubility of NaCl is 20.25%.) Advantage is taken of this difference in solubility to separate the two substances. The disadvantage of fractional crystallization is the high energy requirement. For this reason other methods of separation are more commonly used today.

In addition to the primary elements found in fertilizers (N, P, and K), the secondary elements Ca, Mg, and S as well as micronutrients (*e.g.*, Fe, Mn, Mo, and B) are needed for plant growth. "Lime", usually in the form of $CaCO_3$, is frequently applied to acid soils to raise the pH and is a source of calcium. Dolomitic limestone (a mixture of $CaCO_3$ and $MgCO_3$) is a source of both Ca and Mg. Sulfate salts, including superphosphate, are sources of sulfur for soils deficient in this element. Micronutrients are also added to fertilizers to improve plant growth.

Metallurgy, extraction of metals from their ores, is an important facet of industrial chemistry. There are several general methods used in the production of metals from their ores. All involve the reduction of metal compounds, since very few metals are found free (uncombined) in nature. The most reactive metals require electrolytic reduction, whereas, less reactive metals may be reduced chemically by such reducing agents as C, CO, or H_2. Because C is inexpensive and readily available (as coke), carbon is used directly or partially oxidized to CO and reacted with metal oxides at high temperatures to form CO_2 and the free molten metal. Iron is produced by this method.

$$Fe_2O_3(s) + CO(g) \rightarrow Fe(l) + CO_2(g)$$

Some metals, such as cobalt, germanium, and tungsten, are reduced chemically by hydrogen to give the metal. As mentioned above, hydrogen is produced from natural gas and petroleum products, a more expensive process than carbon reduction used only if less expensive reducing agents are unavailable or if undesirable products result when other reduction methods are used.

The more reactive metals, such as aluminum and the alkali and alkaline earth metals, must be produced electrolytically. Bauxite, the principal aluminum ore, contains hydrated aluminum oxide. Impurities are removed from the ore by dissolution of Al_2O_3 in NaOH, dilution to precipitate $Al(OH)_3$, and dehydration to Al_2O_3.

$$Al_2O_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$$
$$Al(OH)_4^-(aq) \rightarrow Al(OH)_3(s) + OH^-(aq)$$
$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$$

Aluminum is produced by the electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6 (cryolite) using carbon electrodes. The electrode reactions are:

Anode: $C + 2O^{2-} \rightarrow CO_2(g) + 4e^-$

Cathode: $Al^{3+} + 3e^- \rightarrow Al$

(Note that the carbon anode is consumed during electrolysis.) This process for the production of aluminum was developed independently by Charles Hall in the United States and Paul-Louis Héroult in France in 1886 (see *History*).

Because of the expense of using electricity in aluminum production and the fact that aluminum does not readily oxidize like iron on exposure to air, extensive efforts are being made to recycle aluminum. The cost of recycling aluminum is 5% of the cost of producing aluminum from bauxite ore. This fact has led to a significant increase in the recycling of aluminum. In 1972, only 15.4% of the aluminum beverage cans produced were recycled. By 1982, 55.5% of the aluminum beverage cans produced were recycled. Aluminum is also reclaimed from automobile parts and construction materials.

A discussion of industrial chemistry must include reference to the distinction between chemical reactions as carried out in the laboratory and industrial processes. Prior to 1900, most industrial processes were "batch" processes involving the same reactions used in the laboratory, but on a larger scale using larger containers. When a reaction is carried out on a large scale sometimes the course of the reaction is changed by introducing different conditions, such as the generation of excessive quantities of heat that is not effectively dissipated because of poor heat exchange or altering the rate of reaction, making a batch process impractical. Sometimes the starting materials for laboratory-scale reactions are too expensive to be practical industrially, but different, less-expensive raw materials can be used to prepare the desired product using a different reaction. This different reaction may involve more steps or reaction conditions that are impractical in the laboratory, but economic considerations are the driving force in selection of processes for industrial chemical syntheses. Today most industrial processes are continuous or semi-continuous, many being carried out under much different conditions and generally employing a different reaction from those a chemist would use in the laboratory. The continuous process has contributed to reduction in cost of many chemicals and has increased large scale synthesis of many important chemicals.

In "scaling up" from laboratory scale to commercial scale several steps are required. After the reaction conditions have been optimized on the laboratory scale, the reaction is tried in a small-sized model of the industrial process. After this, a large-sized or developmental unit is utilized to optimize reaction conditions. The process is then ready for semi-commercial plant scale and finally is adapted for the full-scale commercial plant. Computer simulation is used for modeling the process as a means of predicting potential problem areas. Computer modeling also assists in designing the lay-out and control systems for large-scale plants. Throughout the process of scaling up, the industrial chemist works closely with engineers to monitor production and product quality. Frequently, reactions that occur readily and with good yield on a laboratory level must be significantly modified for industrial-scale conditions. Sometimes the reaction itself must be modified or a completely different reaction used. Sometimes the reaction conditions or plant design can be adapted. In either case, a knowledge of chemistry as well as the principles of engineering is essential to the development of a successful industrial process.

Language of Chemistry

1. Historically lime meant calcium oxide, CaO (also called "quicklime" or "burned lime"). Slaked lime (or "hydrated lime") refers to calcium hydroxide, $Ca(OH)_2$. In the fertilizer industry, lime is used to refer to both of these substances and to other calcium or magnesium salts of weak acids, such as calcium carbonate, $CaCO_3$:

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$$

2. "Sour" petroleum or natural gas contains H_2S or sulfur-containing hydrocarbons.
3. Superphosphate (sometimes called superphosphate of lime) is a mixture of $Ca(H_2PO_4)_2$ and $CaSO_4 \cdot 2H_2O$ formed by the reaction:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4 \cdot 2H_2O$$

4. Triple superphosphate (sometimes called triple superphosphate of lime) is $Ca(H_2PO_4)_2$ formed by the reaction:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

Names of relevant commercial processes:

5. In the Claus process, sulfur is produced by oxidation of H_2S in "sour" natural gas and petroleum products.
6. In the Contact process for sulfuric acid, SO_2 is oxidized to SO_3 in the presence of V_2O_5 catalyst. SO_3 is dissolved in H_2SO_4 and the resulting $H_2S_2O_7$ is hydrolyzed or diluted to produce H_2SO_4.
7. The Frasch process is one method of obtaining sulfur from native deposits. Super-heated water and compressed air are forced into the underground deposit to melt the sulfur and bring it to the surface, where it is collected in almost pure form.
8. The catalyzed reaction of nitrogen and hydrogen to produce ammonia at high pressure (200 atm) and temperature (500 °C) is known as the Haber-Bosch process.
9. The Hall process is an electrolytic method for production of Al from bauxite ($Al_2O_3 \cdot 2H_2O$). After a pretreatment process to remove some impurities such as iron compounds, Al_2O_3 dissolved in Na_3AlF_6 is electrolyzed between carbon electrodes to produce Al and O_2, which reacts with the carbon anode to produce CO and CO_2.
10. In the Ostwald process, nitric acid is made by the oxidation of NH_3 to NO followed by oxidation of NO to NO_2 and dissolution of NO_2 in water to give HNO_3.

Common Student Misconceptions

1. **"Algal bloom from fertilizer run-off *produces* oxygen."**

   Actually algal bloom from fertilizer run-off reduces the oxygen content of the water rather than enhances it (as expected, since algae produce O_2 by photosynthesis). The algae block sunlight to plants below them. These plants and the organisms that depend on them die and decay. This increase in decay uses O_2 at a faster rate than the algae can produce it.

2. **"The main use of NH_3 is in household cleaners (or maybe chemistry laboratories)."**

   Most ammonia is used in the fertilizer industry; however, there are many industrial uses for NH_3. Use of ammonia in household cleaners constitutes a very minor use for ammonia.

3. **"Most of the H_2SO_4 produced industrially is used in chemistry laboratories."**

   H_2SO_4 is one of the most important industrial chemicals and is used in the fertilizer industry as well as in other commercial processes. (Examples are the paper industry, paints and pigments, refineries, metal plants, *etc.*)

4. **"The use of fertilizers is 'bad'."**

   Although 'organic gardening' has increased and new farming methods are being developed and encouraged that utilize "natural fertilizers" (*e.g.*, no-till farming), the world's food needs cannot presently be met without the use of commercial fertilizers. It is important to emphasize the close link between food production and the use of commercial fertilizers.

5. **"All industries are big contributors to pollution."**

   Most industries try to work out chemical reactions and production protocols for the least polluting method.

6. **"Chemical industries are an unsafe environment in which to work."**

   Chemical industries have a high safety record. Working in the chemical industry is no more dangerous than in any other industry.

Problem Solving

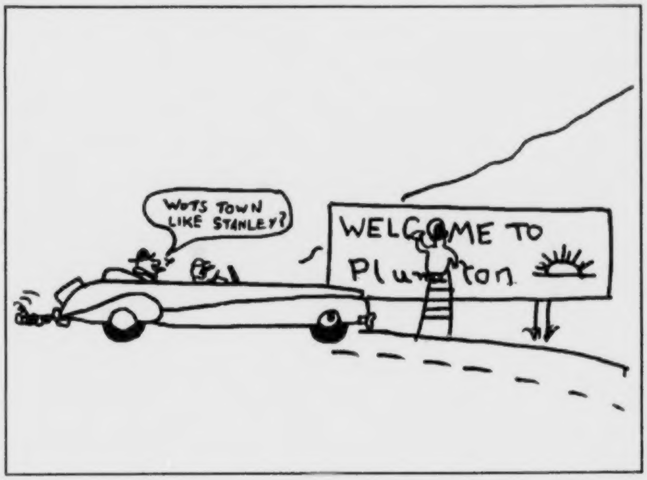
1. This is a good place to review balancing equations, stoichiometry, equilibrium, *etc.* It is important to emphasize the relationship of chemistry to other disciplines in discussing this material with students.
2. This fictitious case history illustrates the impact of chemistry on society by outlining the factors to be considered in locating an industry: lead smelting.

   Problem

   Imagine that you are the managing director of a chemical firm that extracts lead metal from its ore, lead sulfide (galena). A new smelter is to be built in the small coastal town of Plumbton, and a number of sites, lettered A to E on the map (shown at the end), have been proposed by the local council.

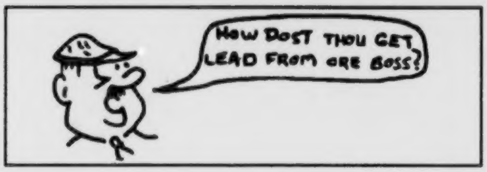
   What are the good and bad points of each site? As managing director, which site would you choose? To help you arrive at a decision, an information sheet about Plumbton and lead smelting is given that must be completed first.

EH! BOSS, WHERE IN PLUMBTON ARE YOU GOING TO BUILD T' SMELTER?
DON'T KNOW STANLEY. BEST TAKE LOOK.



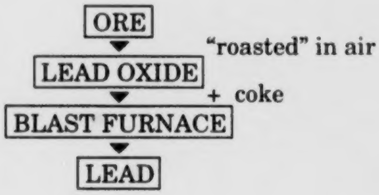
Plumbton

Plumbton is a coastal town with a population of 60,000 situated in an area of outstanding natural beauty. In the recent past, its main industry was fishing, and it is still well known for its oysters. More recently tourists have provided most of the town's employment, but this is only seasonal, and the town's unemployment figures are 10% above the national average. The only light industry is a small factory manufacturing lead-acid car batteries.


HOW DOST THOU GET LEAD FROM ORE BOSS?

Lead Smelting

In this process, lead sulfide (the ore galena) is changed into lead oxide by heating strongly in plenty of air ("roasting" it with plenty of oxygen). Lead metal is obtained from lead oxide by a process of reduction similar to that used in the extraction of iron. The lead oxide is mixed with carbon in the form of coke and heated in a current of hot air in a blast furnace.



Write out and answer the following questions:

1. What is the common name of the ore from which lead is extracted? *[Galena]*
2. Write an equation to show what happens when the ore is roasted. $[2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)]$
3. Name the waste product formed in this reaction. *[Sulfur dioxide gas]*
4. What is meant by the word *reduction*? *[Gain of electrons]*
5. Write an equation to show how the lead oxide is reduced. $[2PbO(s) + C(s) \rightarrow 2Pb(s) + CO_2(g)]$
6. What is the reducing agent in this reaction? *[Coke, C]*
7. What is the waste product in this reaction? $[CO_2(g)]$

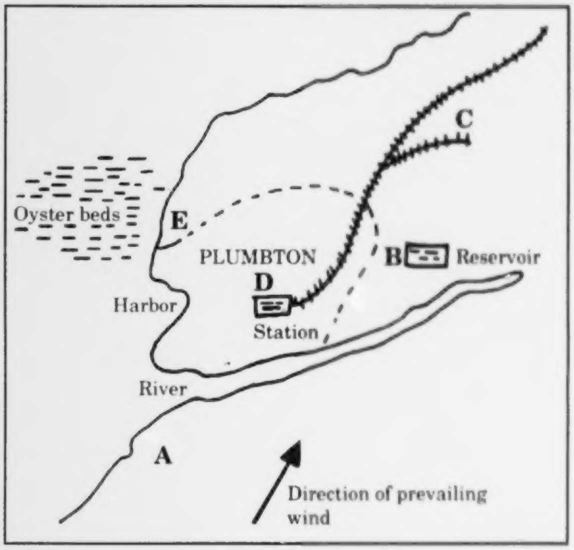
As well as the waste products listed above, there is also solid waste called *slag* that has to be disposed of by the company.

Points to Consider

1. Society needs lead (to make lead-acid batteries, for example).
2. Profit and employment
3. Transport ... large amounts (about one million tons) of galena and coke will have to be brought into the town by rail or boat, and similarly the lead will have to leave the town.
4. Nearness to the town...
   a. for convenience of the work force, but
   b. an industrial site within an urban area may disturb local residents.

5. Removal of *all* waste products.
6. Pollution. Lead is a poisonous element. There will be some lead in the solid waste, and despite strict controls some lead may escape into the atmosphere from the blast furnace; this may combine with other gases in the atmosphere and rainwater, thus entering streams, the river, and the sea.

   Oysters do not suffer from lead poisoning but can store large quantities of lead in their bodies. Humans can take in lead directly from the atmosphere or by eating contaminated food.



WHAT'S THEM LETTERS FOR?
NEW SMELTER, FLO, GIVE US 'NOTHER GLASS
Pb

Study the map and the points to consider when choosing a site; then complete the following table in your notebook.

SITE	ADVANTAGES (for)	DISADVANTAGES (against)

As managing director, which site would you choose? *[C]*

Why? *[Site C is upwind from the town.]*

What other factors would you take into account? *[If Site C is higher elevation than the town, contamination of the water table could occur.]*

CHEM 13 NEWS, December 1980, p. 10.

Decision Making

Students can assume they are managers in a chemical manufacturing plant and discuss factors to be considered in their responsibilities to their employer and society. Factors include: alternative manufacturing processes (different chemical reactions with different starting materials to produce the same product—stoichiometry and energy consumption as well as economics are important issues here), source and consumption of raw materials (including possible exploitation of natural resources of underdeveloped nations), pollution and waste disposal and public health issues. Students should be guided to see that there is not a simple "right answer." As with other decisions in our lives there are tradeoffs. As responsible citizens, we must make informed decisions concerning complex issues. The study of chemistry helps us prepare to make those decisions.

Pollution problems, waste disposal problems, *etc.*, facing our communities and nations are linked to consumer use of chemical products (*e.g.*, fertilizer run off, waste water treatment, recycling paper and metals) as well as to commercial production of chemicals. It is important that students realize that chemical reactions can be used to change the form of matter but that it is impossible to make pollution or waste "disappear." Factors that must be considered in addition to the feasibility of the process are the cost (economics), the environmental effect of the clean-up, public perception of the problem and the proposed solution.

HISTORY: ON THE HUMAN SIDE

1. Although one of the most abundant metals, aluminum was considered a precious metal until the late 1800s. Many chemists tried to find a practical method for isolating aluminum from its ores, but it was 1886 before Charles Martin Hall, in Oberlin, Ohio, and Paul Héroult, in France, independently discovered the same method for electrolytic reduction of aluminum from bauxite ore. Both of these men were only 22 years old when they made this discovery. Hall went on to found the Aluminum Corporation of America (ALCOA). In a day when aluminum beverage cans present a litter problem along our highways, it is difficult to believe that before the 1880s aluminum was more precious than gold!

2. Fritz Haber first prepared ammonia from its elements in 1903, but years of experimentation were required before the synthesis became practical on an industrial scale. In 1908, he approached BASF regarding financial backing to develop his ammonia synthesis for industrial production. Carl Bosch, an engineer, was assigned to help him optimize conditions to facilitate the industrial synthesis of ammonia from nitrogen and hydrogen. There were several problems faced in adapting Haber's synthesis to an industrial scale. The osmium catalyst Haber used in the laboratory scale reaction was rare and difficult to handle. After much experimentation an iron catalyst containing oxides of aluminum, potassium, and calcium was found suitable. The catalyst is now generated *in situ* by the hydrogen reduction of Fe_3O_4 containing small amounts of the other oxides. Because high pressures were required, new equipment had to be developed. In 1913, the first plant opened. Essentially the same process is used today. The industrial synthesis of ammonia from the elements is frequently called the Haber process, but should be referred to as the Haber-Bosch process. Haber developed the reaction on a laboratory scale, but Bosch translated it into an industrial process.

3. In the early 1950s most large refineries were installing catalytic reformers for improving the octane number of their gasoline. Catalytic reforming units could convert low octane gasoline to high octane gasoline in a single pass over a platinum-based catalyst.

$$\underset{\substack{\text{Heptane}\\(\text{Octane number} = 0)}}{C_7H_{16}(l)} \xrightarrow[\text{Heat}]{\text{Catalyst}} \underset{\substack{\text{Toluene}\\(\text{Octane number} = 103)}}{C_7H_8(l)} + 4H_2(g)$$

Along with the aromatic products, catalytic reformers produced huge amounts of hydrogen (four moles per mole of aromatic hydrocarbon). There was some demand for hydrogen, but not for the enormous amounts that were rolling out of these hydroformers. Most of the hydrogen was burned off in giant flares.

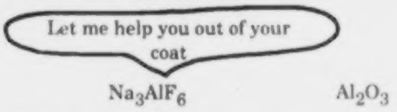
Refiners needed a use for all that hydrogen. After looking into various ways to use hydrogen, the production of ammonia looked most promising. Ammonia could be used as fertilizer, a large-volume product. Farmers at that time were using only solid fertilizers and would not know how to handle ammonia. Although refiners could use ammonia to make ammonium nitrate, ammonium sulfate, or ammonium phosphate, why not put ammonia directly into the soil? The refiners convinced farmers that they could improve yields by fertilizing with liquid ammonia solution, or even with pure anhydrous ammonia. They succeeded in selling farmers on fertilizing with ammonia and needed to increase the size of their ammonia plants to meet the new demand. Consequently, new plants had to be built to make more hydrogen from natural gas, by steam reforming.

$$CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$$

4. In the early 1900s, Wilhelm Ostwald developed a method of producing nitric acid starting with ammonia. The oxidation of ammonia using a platinum catalyst had been reported earlier by Charles Frederic Kuhlmann in France. Ostwald perfected the process and obtained patents in several countries, but Germany refused to grant him a patent. Prior to World War I, Germany had stockpiled Chilean nitrate of soda ($NaNO_3$) apparently intending to use an older method to prepare nitric acid (needed for the manufacture of gunpowder) by distilling nitric acid from a mixture of sodium nitrate and sulfuric acid.

HUMOR: ON THE FUN SIDE

1. Message on bumper stickers:
   a. Don't like farmers? Don't complain with your mouth full.
   b. What in the world isn't chemistry?
2. **CHEMTOON**


Let me help you out of your coat
Na_3AlF_6
Al_2O_3

CHEM 13 NEWS, December 1983, p. 16

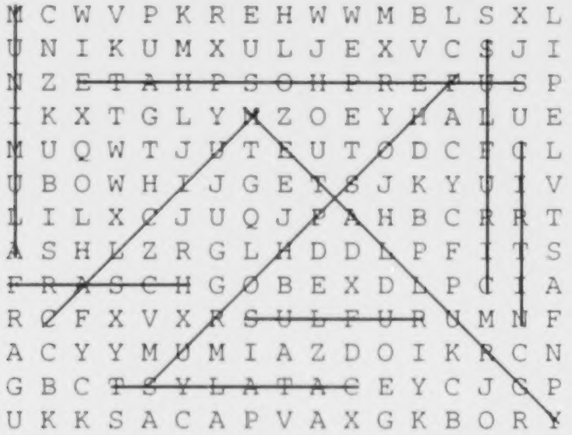
3. A chemistry student from Birmingham
Found his shirt cuffs so handy, he cribbed on 'em;
But the elements ran
As he wrote his exam
Forming steel from Fe, C, and molybdenum.

Adapted from *CHEM 13 NEWS, March 1965, p. 882*

4. Oxide: a favorite substance for making shoes.

CHEM 13 NEWS, November 1976, p. 1106

5. Word Search (see *Appendix* for master copy)



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M C W V P K R E H W W M B L S X L
U N I K U M X U L J E X V C S J I
N Z E T A H P S O H P R E P U S P
I K X T G L Y M Z O E Y H A L U E
M U Q W T J U T E U T O D C F C L
U B O W H I J G E T S J K Y U I V
L I L X C J U Q J P A H B C R R T
A S H L Z R G L H D D L P F I T S
F R A S C H G O B E X D L P C I A
R C F X V X R S U L F U R U M N F
A C Y Y M U M I A Z D O I K R C N
G B C T S Y L A T A C E Y C J G P
U K K S A C A P V A X G K B O R Y
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Quicklime, burned lime, or just lime—its the oxide of this metal.
2. Process of extracting sulfur through use of superheated water and compressed air.
3. Acid made from the Ostwald process.
4. A mixture of $Ca(H_2PO_4)_2$ and $CaSO_4 \cdot 2H_2O$.
5. A complete fertilizer contains the elements nitrogen, potassium and this element.
6. An oxide of vanadium serves this function in the Contact process.
7. This acid is the substance produced in largest quantities in the United States.
8. Process of extraction of metals from their ores.
9. This metal is obtained from bauxite.
10. Sour petroleum or natural gas contains compounds of this yellow solid.

Answers: 1. CALCIUM 2. FRASCH 3. NITRIC 4. SUPERPHOSPHATE 5. PHOSPHORUS 6. CATALYST 7. SULFURIC 8. METALLURGY 9. ALUMINUM 10. SULFUR

6. See relevant cartoons at end of module.

MEDIA

Because it is impossible to demonstrate industrial processes adequately in the classroom, it is strongly recommended that you obtain videos or films of industrial processes to view with your class. A few of these are listed below:

1. The *World of Chemistry* videotapes "No. 16: The Busy Electron," "No. 17: The Precious Envelope," "No. 18: The Chemistry of the Earth," "No. 19: Metals," "No. 20: On the Surface," and "No. 25: Chemistry and the Environment" are particularly appropriate for this module. World of Chemistry Videocassettes. Annenberg/CPB Project, P.O. Box 1922, Santa Barbara, CA 93116-1922; (800) 532-7637; World of Chemistry Series, Atlantic Video, 150 South Gordon Street, Alexandria, VA 22304; (703) 823-2800 or QUEUE Educational

Video, 338 Commerce Drive, Fairfield, CT 06430; (800) 232-2224.

2. *Chemical Equilibrium*, Program 6 of TV Ontario Videotape Series. This tape highlights the Haber Process. Free previews are available from TV Ontario Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516; (919) 380-0747.
3. "Chemistry in Action" Videotape Series is published by Films for the Humanities and Sciences, P.O. Box 2053, Princeton, NJ 08543; (800) 257-5126.
    - a. *Aluminum* (#NB-1108).
    - b. *Chemicals from NaCl* (#NB-1110).
4. Software published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
    - a. *Lake Study* for Windows, by David Whisnant and James McCormick. Vol. V B, No. 1, for IBM PS/2, PC-compatible computers.
    - b. *BCTC* for Windows, by David Whisnant and James McCormick. Vol. V B, No. 2, for IBM PS/2, PC-compatible computers.
5. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).
    - a. For the Apple II computer running on ProDOS: AR 801, AR 802.
    - b. For the Apple II computer: AP 801, AP 803, AP 805, AP 806, AP 807.
    - c. For IBM PCs and PC-compatibles: PC 3702, PC 3702, PC 3705.
    - d. For the Apple Macintosh computer: MC 801.
6. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
    - a. "Making Aspirin," "Perkin's Experiment," and "Making Polyethylene," three chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc II (double sided, 60 min.), Special Issue 4.
    - b. "Polymers," and "Dyes," two chapters on the videodisc *Demonstrations in Organic Chemistry* (double sided, 60 min.), Special Issue 6.

INSTRUMENTATION

A simple electrolysis apparatus is described in *Demonstration 3*.

A simple conductivity apparatus is described in the articles by Gadek (1987) and Russo (1986) in the *References* section.

Almost all topics are related to this module: acids and bases, balancing equations, chemical equilibrium, descriptive chemistry of elements, electrochemistry, kinetics, mole, redox reactions, stoichiometry, and thermochemistry.

Links/Connections

WITHIN CHEMISTRY

Almost all topics are related to this module: acids and bases, balancing equations, chemical equilibrium, descriptive chemistry of elements, electrochemistry, kinetics, mole, redox reactions, stoichiometry, and thermochemistry.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

Biology

A natural connection is the use of artificial nitrates from fertilizers to supplement the usable nitrates in the soil. Since most plants are not legumes and consequently incapable of fixing nitrogen, they must have a source of nitrate to insure proper growth and production needs are met. Removal of plant materials from farming areas greatly reduces the return of nitrates made from ammonia or ammonium salts by bacteria. Approximately 10% of nitrates added to the soil each year are artificial fertilizers, while the remainder is a result of nitrogen fixation by symbiotic bacteria in the nodules on roots of legume plants.

$$2\,NH_3(g) + 3\,O_2(g) \rightarrow 2\,NO_2^-(aq) + 2\,H^+(aq) + 2\,H_2O(l)$$

$$2\,NO_2^-(aq) + O_2(g) \rightarrow 2\,NO_3^-(aq)$$

The oxidation of ammonia (or ammonium ion) is an exergonic process, and the energy released is used by bacteria as a primary energy source.

Earth Science

Metallurgy results in the production of useful and needed materials for industry. Most metals are not readily available but are also contained in ores with many other materials that must be eliminated. Major metals and their sources are shown in the following chart.

Metal	Mineral	Composition
Al	Bauxite	Al_2O_3
Cr	Chromite	$FeCr_2O_4$
Cu	Chalcocite	Cu_2S
	Malachite	$Cu_2CO_3(OH)_2$
Fe	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
Pb	Galena	PbS
Mn	Pyrolusite	MnO_2
Mo	Molybdenite	MoS_2
Hg	Cinnabar	HgS
Sn	Cassiterite	SnO_2
Ti	Rutile	TiO_2
	Ilmenite	$FeTiO_3$
Zn	Sphalerite	ZnS

Since the United States is dependent on the availability of such metals, these metals are considered strategic. As a result, these metals are stockpiled.

Obtaining metals from their ores involves several steps: (1) mining, (2) preparing the ore by concentrating it, (3) reducing the metal ions in the ore to produce the free metals as atoms, (4) refining or purifying the metal, and if needed (5) producing alloys. Every metal has its own unique processes and reactions involving these steps.

Chemical Engineering

Commercial chemical manufacturing processes such as the Contact, Ostwald, and Haber processes involved in fertilizer production.

Materials Engineering

A major consideration in construction is the strength of the alloys used. A natural consequence of metallurgy is the study of ductility, tensile strength, conductivity, *etc.* associated with alloys.

TO THE CONTEMPORARY WORLD

Personal

Possible careers are agronomist, chemical engineer, environmental scientist or environmental hygienist, industrial chemist, recycling engineer (resource management), research chemist, sanitation or water chemist, soil scientist, metallurgist.

Community

1. **Field trips**: agricultural extension service, chemical manufacturing plant, environmental testing lab, health department, industrial chemical sales company
2. **Knowledgeable individuals**: agronomists, chemical engineers, environmental scientists (environmental hygienists), industrial chemists, pharmacists, recycling engineers (resource management), research chemists, sanitation department chemists, water chemists, soil scientists, metallurgist

SOCIETAL (SCIENCE/ TECHNOLOGY/ SOCIETY)

Fertilizer run-off is an environmental problem generated by the use of fertilizers to increase food production.

Food production *versus* world economy is an important issue related to this module. Fertilizer use increases food production and is therefore directly related to the economy of a country. Use of fertilizers and subsequent environmental impact *vs.* food production needs should be discussed. Furnishing fertilizers to underdeveloped countries and education of those involved in farming concerning the proper use of fertilizer are important issues.

In spite of extensive production in a few less-industrialized nations, sulfuric acid production is still considered by many to be one of the ten leading economic indicators. Ammonia is also important to national economy. A comparison of production of various substances and national prosperity is an interesting exercise that provides an opportunity for students to see that elements and compounds they have studied are directly related to current economic issues.

The danger of ammonium nitrate (there are frequent reports of fires caused by improper use or storage) or other chemicals can be discussed if newspaper clippings are saved as the accidents occur. Incorrect, or incomplete, explanations that imply chemical errors are frequently given in news accounts. Again if clippings are saved, students will have the opportunity to see that science literacy is important for everyone—including journalists.

Recycling of metals, particularly aluminum, fits logically here. Recycling aluminum is particularly important because of decreasing reserves of bauxite and the need to conserve energy. By recycling one aluminum beverage can, it can save enough energy to burn a 75-W light bulb for three hours. In the United States, 20% of the energy used is consumed in the Hall Process to produce aluminum from bauxite ore.

Extensions

Determination of soil moisture and pH activity can be extended to include a comparison of the soil analyses from different locations.

Compare the effect of different fertilizer formulations (8-8-8 vs. 6-12-6, *etc.*) on plant growth.

Studies have shown that phosphate rock can be used directly as fertilizer. This fact has significant implications for developing nations because it does not require a sophisticated chemical industry to produce fertilizer. Research this idea and, if a source of phosphate rock can be located, students can grow plants using commercial fertilizer (such as superphosphate) and phosphate rock and compare the results (see Worthy, 1986, in *References* section).

Investigate hydroponic plant growth and nutrients needed for different plants. Experiment with growing different plants hydroponically.

Compare the annual production of various industrial chemicals for different countries.

Industrial processes for various substances (*e.g.*, Solvay process for Na_2CO_3, Downs process for sodium, *etc.*) and the lives of individuals associated with industrial processes provide interesting library research topics.

References

Several projects are referred to in the *Societal Links and Connections* section.

Module developed by Caroline L. Ayers, Philip Dail, and Carolyn Morse, the North Carolina team.

The following individuals provided information and/or references used in the preparation of this module:

John Jernigan, Texasgulf, Aurora, NC

James M. Lucas, Applied Statistics Group, E. I. Du Pont de Nemours and Company, Wilmington, DE

Horace Mann, Fertilizer Division, Tennessee Valley Authority, Muscle Shoals, AL

H. Joseph Kleiss, Department of Soil Science, North Carolina State University, Raleigh, NC

Bohn, H. L., McNeal, B. L., and O'Connor, G. A. (1971). *Soil chemistry*. New York, NY: Wiley-Interscience.

This standard soil chemistry text contains information such as acidity of soils, oxidation-reduction processes in soils, and the role of various ions in soil chemistry and plant growth.

Chang, R. (1991). *Chemistry* (4th Ed.). New York, NY: McGraw Hill.

Chapter 26 is devoted to Industrial Chemistry. A table of the top 50 chemicals from 1982-1988 is on p. 1057. The components of petroleum and their uses are shown in a diagram on p. 1055.

Chang, R., and Tikkanen, W. (1988). *The top 50 industrial chemicals.* New York, NY: Random House.

Chemecology.

This magazine, published by Chemical Manufacturers Association (2501 M Street, N.W., Washington, DC 20037, Phone 202-887-1100), is a valuable resource for both teachers and students. Articles on health, safety and the environment are included in each issue. Call or write to obtain issues for use in your classroom.

Chemical and Engineering News.

This news magazine is published weekly by the American Chemical Society and sent to all ACS members. It carries news related to industrial chemistry in each issue. Frequent feature articles describe industrial chemical processes, environmental issues related to industrial chemistry or economic or business issues in chemistry. If you're not an ACS member, find a chemist who is and request back issues for use in your classroom.

Chemical technology: An encyclopedic treatment. (1968). New York, NY: Barnes & Noble.

This reference work contains information about manufacturing processes. Volume 1 contains information about the industrial production of Na_2CO_3.

Faith, Keyes, and Clark's Industrial Chemicals (4th Ed.). (1975). New York, NY: Wiley.

This is a good source of information about industrial chemical processes. For example, the mining and processing of trona are described.

Gadek, F. J. (1987). Easily made electronic device for conductivity experiments. *Journal of Chemical Education, 64,* 628-629.

This article gives directions for a simple conductivity apparatus.

Heitmann, J. A., and Rhees, D. J. (1984). *Scaling up.* Philadelphia, PA: Chemical Heritage Foundation, 3401 Walnut Street.

This pamphlet provides concise information about adaptation of reactions for industrial production. It accompanies a multi-panel traveling exhibit; information regarding the exhibit and its whereabouts can be obtained from CHF.

Hileman, B. (1990, March 5). Alternative agriculture. *Chemical and Engineering News*, pp. 26-40.

The special report includes information on fertilizer consumption by crop as well as pesticide/herbicide use and farming methods. There is also a discussion of government and economic issues related to farming.

International Fertilizer Development Center. *Fertilizer manual.* Muscle Shoals, AL.

This is a revision of *UN fertilizer manual* published in 1967 and contains a history of fertilizers plus information concerning the manufacture of fertilizers.

Jacobs, H. S., Reed, R. M., Thien, S. J., and Withee, L. V. (Eds.). (1971). *Soil laboratory exercise source book.* Madison, WI: American Society of Agronomy.

This reference contains laboratory exercises related to soil chemistry. (Address: American Society of Agronomy, 677 South Segoe Road, Madison, WI 53711)

Jones, M. M., Johnston, D. O., Netterville, J. T., Wood, J. L., and Joesten, M. D. (1987). *Chemistry and society* (5th Ed.). Philadelphia, PA: Saunders.

This text includes a chapter on agricultural chemistry as well as sections discussing various industrial processes. Many references to societal issues related to various chemistry topics are included.

Kirk-Othmer encyclopedia of chemical technology (3rd Ed.). (1978-1984). New York, NY: Wiley.

This 24-volume work provides a wealth of information about industrial processes. Information about the industrial production of Na_2CO_3 is found in Volume 1.

Kleiss, H. J. (1986). *Applications of the basic sciences in soil science.* Raleigh, NC: Author.

This work describes soil science laboratory activities.

New developments in fertilizer technology. (1983). Muscle Shoals, AL: National Fertilizer Development Center, Tennessee Valley Authority.

This contains extensive material on the manufacture of fertilizers. Order from publisher.

Pearson, R. W., and Adams, F. (Eds.). (1967). *Soil acidity and liming.* Madison, WI: American Society of Agronomy.

This work provides information on agricultural studies of the effects of soil acidity and liming on plant growth. Functions and deficiency characteristics in plants for various elements is given.

Reisch, M. S. (1993, April 12). Top 50 chemical production resumed growth last year. *Chemical and Engineering News,* p. 17.

This article lists the top 50 chemicals and quantities produced in the U.S. in 1991, a comparison with production in 1990, and growth over last ten years. A similar article appears each April.

Russo, T. (1986). A low-cost conductivity apparatus. *Journal of Chemical Education, 63,* 981-982.

Construction of a simple conductivity apparatus is described in this article.

Selinger, B. (1989). *Chemistry in the marketplace* (4th Ed.). Marrickville, Australia: Harcourt.

This reference provides information on uses of a wide range of substances. (Can be purchased from ACS Education Office.)

Slowinski, E. J., Wolsey, W. C., and Masterton, W. L. (1984). The Solvay process. In *Chemical principles in the laboratory* (3rd Ed., pp. 85-91). Philadephia, PA: Saunders.

The Solvay Process activity was adapted from the experimental procedure described here.

Tocci, S. (1987). *Chemistry around you.* New York, NY: Prentice Hall.

This book describes chemistry activities suitable for use with students.

Ullmann's encyclopedia of industrial chemistry (5th Ed.). (1985-). Weinheim: VCH.

Extensive information on industrial chemicals and manufacturing processes is contained in this reference. New volumes are published annually. (19 of 36 planned volumes had been published in 1990.)

Worthy, W. (1986, September 22). Fertilizing by ion exchange promising. *Chemical and Engineering News, 64,* 29.

This article describes the use of phosphate rock as fertilizer.

Appendix

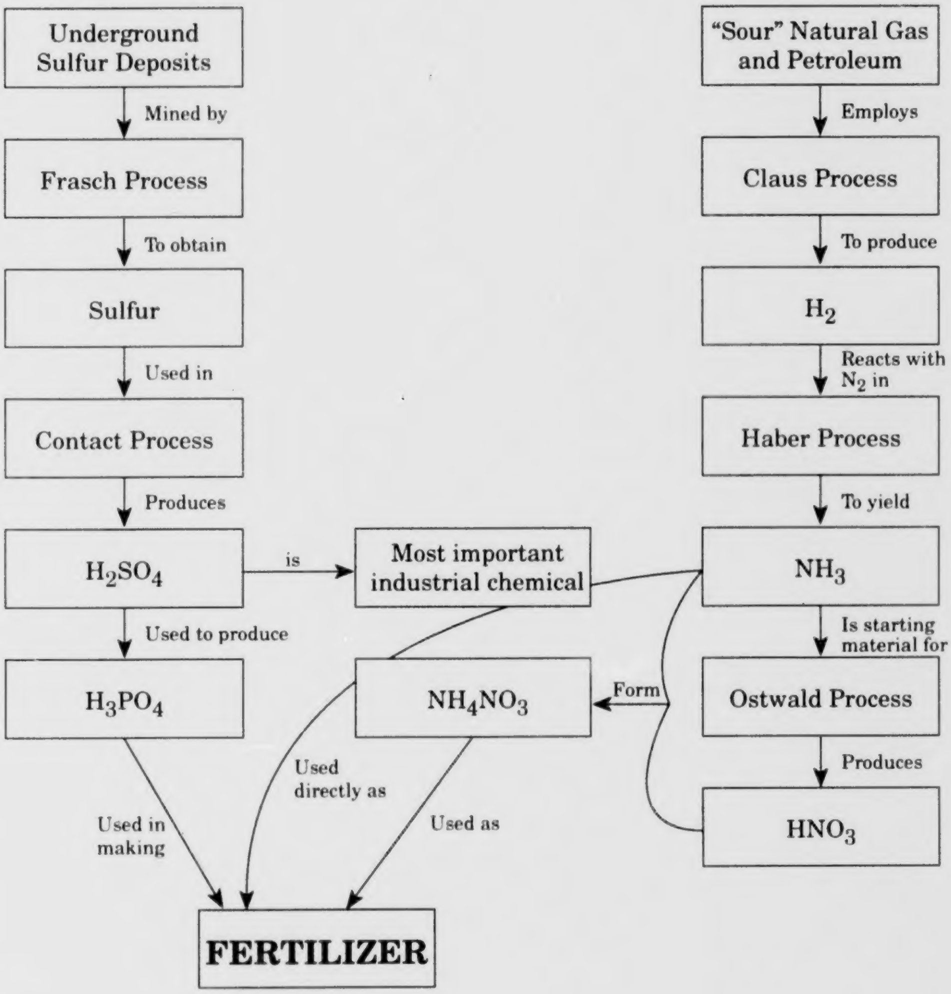
- **Transparency Masters**
  1. Top 50 Chemicals in 1991 and 1992

     This list is taken from a *C&EN* article (Reisch, 1993). An updated list is reported each April, (See *References*).
  2. Interrelation of Industrial Processes in the Fertilizer Industry
  3. Word Search
- **Humor**

Top 25 Chemicals in 1991 and 1992

Rank		
1991	1992	
1	1	Sulfuric acid
2	2	Nitrogen
3	4	Ethylene
4	3	Oxygen
5	5	Ammonia
6	6	Lime
7	7	Phosphoric acid
8	8	Sodium hydroxide
9	10	Chlorine
10	9	Propylene
11	11	Sodium carbonate
12	12	Urea
13	13	Nitric acid
14	15	Ammonium nitrate
15	14	Ethylene dichloride
16	17	Benzene
17	16	Vinyl chloride
18	20	Carbon dioxide
19	19	Methyl *tert*-butyl ether
20	18	Ethylbenzene
21	21	Styrene
22	22	Methanol
23	28	Terephthalic acid
24	23	Formaldehyde
25	27	Toluene

Interrelation of Industrial Processes in the Fertilizer Industry



Word Search

```
M C W V P K R E H W W M B L S X L
U N I K U M X U L J E X V C S J I
N Z E T A H P S O H P R E P U S P
I K X T G L Y M Z O E Y H A L U E
M U Q W T J U T E U T O D C F C L
U B O W H I J G E T S J K Y U I V
L I L X C J U Q J P A H B C R R T
A S H L Z R G L H D D L P F I T S
F R A S C H G O B E X D L P C I A
R C F X V X R S U L F U R U M N F
A C Y Y M U M I A Z D O I K R C N
G B C T S Y L A T A C E Y C J G P
U K K S A C A P V A X G K B O R Y
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Quicklime, burned lime, or just lime—its the oxide of this metal.
2. Process of extracting sulfur through use of superheated water and compressed air.
3. Acid made from the Ostwald process.
4. A mixture of $Ca(H_2PO_4)_2$ and $CaSO_4{\cdot}2H_2O$.
5. A complete fertilizer contains the elements nitrogen, potassium, and this element.
6. An oxide of vanadium serves this function in the Contact process.
7. This acid is the substance produced in largest quantities in the United States.
8. Process of extraction of metals from their ores.
9. This metal is obtained from bauxite.
10. Sour petroleum or natural gas contains compounds of this yellow solid.

"I haven't started on the new project yet . . . I'm still working on something to unclog drains."

© American Chemical Society. CHEMTECH, February 1980, p. 117. Reprinted with permission.

B.C.
by johnny hart
SO YOU'RE DATING A GUY FROM THE FEED STORE.
NOW HOW DID YOU KNOW THAT?
YOU SMELL LIKE 10-15-30.
© 1980 CREATORS SYNDICATE, INC
12-18

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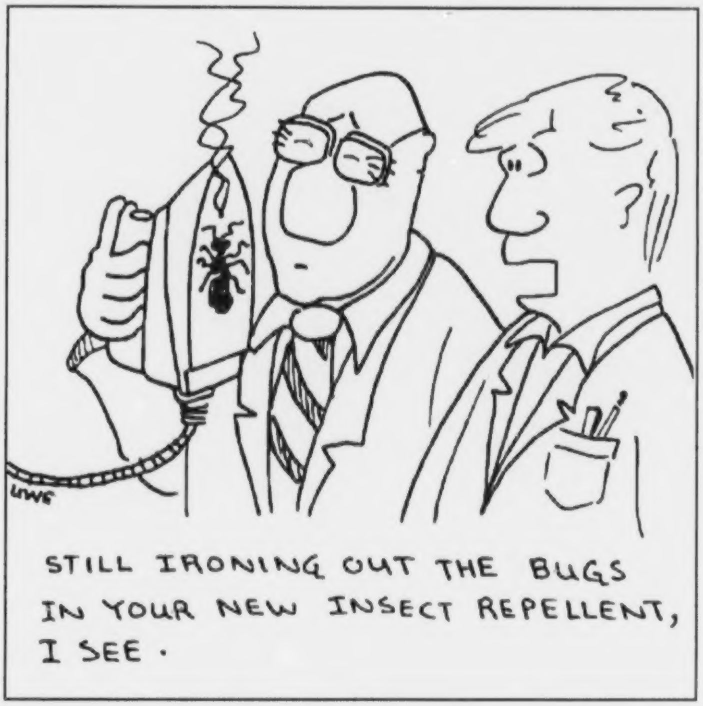
UWE
STILL IRONING OUT THE BUGS IN YOUR NEW INSECT REPELLENT, I SEE.

CHEM 13 NEWS, April 1981, p. 1. Reprinted with permission.

THE WIZARD OF ID
Brant parker and Johnny hart
DO YOU BELIEVE IN REINCARNATION?
IS THAT WHERE YOU COME BACK AGAIN AND AGAIN?
YEP
...WHY NOT?...IT WORKS WITH ALUMINUM CANS
11-14
PARKER
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A SourceBook Module

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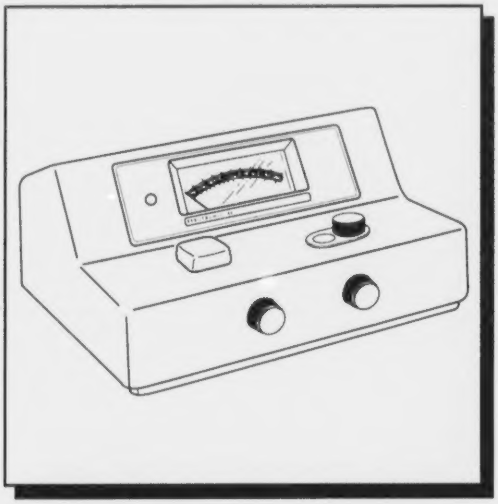
INSTRUMENTATION



ChemSource

Instructional Resources for Preservice and Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

Instrumentation plays an important role in the modern practice of chemistry. It can provide useful information about the structure, identity, and quantity of a substance (see *Chemical Bonding, Molecular Geometry,* and *Organic Chemistry* modules). Very sensitive quantitative instrumental techniques routinely used by chemists have added to our wealth of chemical knowledge. This module will stress the use of spectrophotometry as applied to quantitative analysis.

PLACE IN THE CURRICULUM

Since this module probably does not stand alone in most chemistry courses, it may be partitioned into pieces to fit a particular need. Parts of the material may be used with qualitative analysis, atomic structure, descriptive chemistry, or as enrichment for honor classes.

CENTRAL CONCEPTS

1. An instrument is a tool that allows for physical or chemical characterization of substances by utilizing a variety of probes. The most common probe is electromagnetic radiation.
2. Atomic and molecular species absorb energy in the form of electromagnetic radiation that allows them to undergo certain types of transitions depending upon the energy range of the radiation. Ultraviolet and visible radiation induce electronic transitions, infrared radiation induces vibrational transitions and microwave radiation induces rotational transitions. There is some overlap between the types of transitions induced by the radiation ranges.
3. The behavior of a covalent chemical bond has been likened to the behavior of a spring. Both are capable of stretching and bending. When induced by radiation of specific wavelength, a chemical bond will stretch and/or bend at a frequency corresponding to that of the incident radiation. The absorbed radiation brings about molecular vibrations. Instruments can measure the absorption frequencies and intensities that, when interpreted, can yield information about molecular structure.
4. The relationship between the quantity of radiation absorbed by molecules, the concentration of the molecules, and the path length through which the radiation passes is known as the Beer-Lambert Law. This relationship may be used to determine the concentration of molecules in a solution.
5. Several instrumental methods for determining structures of molecules in solids and gases, ionic solids, network solids (*e.g.*, diamond and graphite), and biologically important substances (*e.g.*, penicillin and insulin) are available and widely used. The more common of these include:
    a. *X-ray diffraction* uses electromagnetic radiation with frequencies near 10^{18} Hz (wavelength 10^{-10} m). When applied to crystalline solids, the method gives conclusive evidence for atomic arrangement, bond angles, and bond distances.
    b. *Electron diffraction* uses the wave characteristics of electrons to provide information about gaseous substances similar to X-ray diffraction information.

c. *Infrared spectroscopy* is used to obtain structural data mainly for noncrystalline molecular species. Infrared radiation causes molecules to vibrate in modes characteristic of their structures.

d. *Microwave spectroscopy* is similar to infrared spectroscopy except that it causes molecules to rotate rather than vibrate, and the method is applicable to a limited number of gaseous molecules.

e. *Nuclear magnetic resonance spectroscopy* utilizes the magnetic properties of atomic nuclei by causing an energy change (change in the direction of nuclear spin) at a characteristic electromagnetic frequency in the radiowave region. This frequency is partly dependent upon the strength of the magnetic field, the nature of the nuclear "magnet," and the arrangement of other nuclei and electrons in the region of the nucleus being studied. The frequencies absorbed reveal the type of nucleus and its chemical environment.

f. *Mass spectroscopy* measures mass to charge ratio for positive ions. Knowing the charge allows the determination of the mass, which, in turn, allows the identification of the substance from the molecular fragments produced.

RELATED CONCEPTS

1. When atoms or molecules lose or gain electrons, they become electrically charged particles called ions. Positive ions (cations) result when electrons are lost, and negative ions (anions) result when electrons are gained.
2. Electrically charged particles follow a circular path when passing through a magnetic field that is perpendicular to the particle's path. The radius of the circular path is directly proportional to the square root of the particle's mass and inversely proportional to the square root of the particle's charge. Measuring the radius and knowing the charge allows determination of the mass.
3. Molecules can absorb electromagnetic radiation and undergo radiation induced rotational, vibrational, or electronic transitions.

RELATED SKILLS

1. Manipulative laboratory skills involving the use of common glassware and hardware are needed to perform the activities.

PERFORMANCE OBJECTIVES

After completing their study of instrumentation, students should be able to:

1. describe the fundamental concepts underlying common instrumentation, including spectrophotometry, X-ray diffraction, and nuclear magnetic resonance.
2. make simple spectrophotometric measurements in the laboratory.
3. describe some of the applications of instrumental techniques, *e.g.*, quality control, consumer protection, pollution monitoring.
4. describe some problem solving applications of instrumentation in research and investigative work.
5. describe some uses of instrumentation in their communities, *e.g.*, water quality testing, sewage treatment, medical applications, *etc.*
6. state some of the vocational and career opportunities available that involve using instrumentation.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Introduction to the Spectrophotometer

Introduction

The spectrophotometer you will use in this activity is an instrument that contains a light source (ultraviolet, visible, or infrared), a diffraction grating monochromator, and a detector. The **light source** produces light of all wavelengths within limits in the ultraviolet and visible regions of the spectrum. The **diffraction grating monochromator** disperses the light into a spectrum and allows successive narrow wavelength bands to pass through a slit to impinge upon a photoelectric detector. The **detector** measures the intensity of light coming from the monochromator.

The **sample holder** lies in the path of the light coming to the detector. When a sample is placed in the holder, the light passes through the sample to the detector. The sample determines whether all of the light, some of the light, or none of the light is transmitted to the detector. Light is absorbed at those wavelengths having the correct energy to cause electronic transitions in the molecules, atoms, or ions in the sample. By measuring the intensity of the light passing through the sample over a range of wavelengths, it is possible to plot the absorption of light *vs.* the wavelength. The resulting plot is the **absorption spectrum** of the sample.

Two kinds of information are obtained from the absorption spectra for substances. First, each substance has its own characteristic absorption spectrum. Thus, the spectrum may be used to identify the substance. Second, the intensity of the absorption can be related to the concentration of the substance in the sample. The Beer-Lambert Law, $A = abc$, allows the determination of the amount (concentration) of the substance in a solution. Here A = sample absorbance; a = absorptivity, a proportionality constant; b = path length; and c = sample concentration.

There are two parts to this activity, qualitative and quantitative spectrophotometry. In the former, the absorption spectrum of chromium(III) nitrate in the visible region (375-700 nm) of the spectrum will be determined. In the latter, a sample of chromium(III) nitrate with unknown concentration will be analyzed. The unknown concentration can be determined by measuring the percent (%) transmittance at the wavelength of maximum absorption and comparing it with a graph (called a concentration curve) of absorbance *vs.* concentration. The % transmittance (%T) is converted to absorbance (A) by the relationship: $\mathbf{A = 2 - \log(\%T)}$; because A is directly proportional to concentration, but %T is not.

Purpose

To determine the absorption spectrum of a solution containing chromium(III) nitrate, $Cr(NO_3)_3$; to determine the concentration of an unknown solution of chromium(III) nitrate.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Chromium(III) nitrate is toxic and is a skin irritant. Avoid contact with this compound and wash hands thoroughly after use.
3. Handle reagent bottles carefully. Always replace the top or stopper after obtaining a reagent.

Procedure

Part I. Qualitative Spectrophotometry

Your teacher will demonstrate the operation of the spectrophotometer you will use. The procedure below is written for the Spectronic 20® with a dial meter.

1. Prepare a data table to record wavelength, percent transmittance data and absorbance. (It would be good to do this before coming to laboratory.) The data table should have three columns headed:

Wavelength (nm)	**%Transmittance (%T)**	**A**

2. If the spectrophotometer is off, then turn the instrument on and allow about 20 min for it to warm up. After warm up, with the sample holder cover closed, set the wavelength dial to 375 nm and adjust the meter to read 0% transmittance with the amplifier control knob (left knob).
3. Obtain two 13-mm x 100-mm test-tubes made of borosilicate glass. The test-tubes must be clean and the outside must be dry and free of fingerprints or smudges. Use lint-free tissue to wipe the outside of the test-tubes. Check to be certain the test-tubes are clean. Put distilled water in both tubes to within 2 cm of the top. In the next step, optical properties of the two tubes will be compared.
4. Check to see that the meter reads 0% transmittance. If it does not, adjust the amplifier control to zero the meter. The test-tubes must always be oriented in the same direction. To insure this, use the frosted or painted area at the top of the tubes to align with the mark on top of the sample holder. Place one of the test-tubes in the sample holder pushing it down until it stops and close the cover. Use the light control knob (right knob) to set the meter to 100% transmittance. Remove the test-tube and read the meter. If it reads 0% transmittance, then you are ready to proceed. If it does not, then readjust the amplifier control knob so the meter reads 0% and then readjust the light control knob once again to read 100% with the test-tube in place. Repeat this step until stable 0% and 100% readings occur. Remove the test-tube and insert the other tube. It should read 100% also. If it reads more than 100%, use it as the blank tube and the first one as the sample tube. Mark the tubes B and S so as not to confuse them. Put the blank tube (B) in a test-tube rack and pour out the water from the sample tube (S).
5. Rinse S twice with a small amount (about 1 mL) 0.020 M $Cr(NO_3)_3$ solution. Discard the rinses into a 150-mL beaker, *not into the sink!* Add 0.020 M $Cr(NO_3)_3$ to the test-tube so that it is about three-fourths full. This same solution will be used for all subsequent readings made in *Part I* of the activity.
6. Zero the instrument if the meter does not read zero. Use the blank tube with distilled water to set 100% transmittance. Remove the blank and insert the sample tube with the chromium(III) nitrate solution. Without adjusting any knobs, read the percent transmittance and record it along with the wavelength in the data table. Remove the sample tube from the holder and place it in a test-tube rack.
7. Turn the wavelength dial to 400 nm and zero the instrument. Place the blank tube in the holder and adjust the meter to 100% transmittance with the light control knob. Remove the blank tube and insert the sample tube again. Read and record the % transmittance in the data table for 400 nm.

8. Continue the procedure of setting 0% transmittance, setting 100% transmittance, and measuring the % transmittance of the chromium(III) nitrate solution at 405, 415, 425, 440, 455, 470, 490, 500, 520, 530, 540, 550, 570, 580, 600, and 625 nm. Remember to record the data collected in the data table.
9. Unless otherwise directed by your teacher, return the chromium(III) nitrate to the reagent bottle from which it was obtained. Follow directions from your teacher in this regard. Pour the small amount of chromium (III) nitrate used to rinse the test-tube from the 150-mL beaker into the receptacle designated by the teacher.
10. Thoroughly wash your hands before leaving the laboratory.

Part II. Quantitative Spectrophotometry (Optional)

Specific directions will be given about whether this part of the activity will be done.

1. Prepare a data table to record the wavelength, percent transmittance, and absorbance for the unknown sample. The unknown is in a stoppered test-tube. Record the unknown identifier on the data table.
2. Measurements on the unknown will be made at the wavelength where the maximum absorption (lowest % transmittance) occurred. This information may be obtained from the data table or furnished by your teacher.
3. Measure the absorbance for the unknown in the same manner as in *Part I*. However, in this case only one measurement will be made. Record the wavelength and absorbance of the unknown.
4. Pour the unknown back into the sample test-tube and return it as instructed by your teacher.
5. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Convert all measured % transmittances to absorbance values in your data table using the conversion table supplied by your teacher.
2. On a piece of graph paper, plot absorbance (A) on the vertical axis *vs.* wavelength (λ) on the horizontal axis. Connect the points to make a smooth curve. This curve is the visible region absorption spectrum of $Cr(NO_3)_3$.
3. *OPTIONAL:* Use the provided calibration curve to determine the concentration of the unknown sample of $Cr(NO_3)_3$. Report the concentration in the laboratory writeup.

Implications and Applications

1. At what wavelengths does $Cr(NO_3)_3$ absorb the maximum amount of radiation?
2. To what colors of light do the wavelengths of the absorption maxima correspond? (It may be necessary to refer to a table of complementary colors or to a diagram of the visible light spectrum.)
3. When a solution is red, does it absorb or transmit red light wavelengths?
4. Give two uses of an absorption spectrum.
5. Colored substances absorb light in the visible region of the spectrum. What is the cause of these absorptions?
6. Instruments are often considered as extensions of human senses. In this sense, what does a visible spectrophotometer do?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Introduction to the Spectrophotometer

Major Chemical Concept

The quantity of light absorbed by a solution is commonly expressed either in terms of *percent transmittance (%T)*, as in *Part I* of this activity, or in terms of *absorbance (A)*. Absorbance is defined as:

$$A = \log_{10}\frac{I_0}{I} = \log_{10}\frac{1}{T}$$

Transmittance (T) is usually expressed as %T = T x 100%, although it actually is defined as:

$$T = \frac{I}{I_0}$$

I_0 is the incident light and I is the transmitted light. Absorbance may be obtained from %T by the equation: $A = \log_{10}(100) - \log_{10}(\%T) = 2 - \log_{10}(\%T)$

This last equation is used to convert %T to A. The absorbance scale is a logarithmic scale. As absorbance increases, scale markings get closer together, and the meter becomes more difficult to read. Thus it is frequent practice to read %T and convert to A. For convenience a table showing %T and the corresponding absorbance (A) is included in the *Appendix*.

For quantitative work the absorbance is more useful than the transmittance because it is directly proportional to concentration. The relationship is known as the Beer-Lambert Law and is: $A = abc$

where a (molar absorptivity or extinction coefficient) is a constant for a given absorbing chemical species, b is the radiation path length through the sample (measured in cm), and c is the stoichiometric molar concentration (mol/L) of the absorbing species. Thus for a given absorbing species at a specific wavelength in a given sample holder of fixed path length (b), a plot of A versus concentration is a straight line if the Beer-Lambert Law is obeyed.

To determine if the Beer-Lambert Law is obeyed over a given concentration range by a given species, measure absorbance as a function of concentration, using the same test-tube for all of the measurements. Plot absorbance *vs.* concentration; check the linear nature of the curve. If the curve is linear, then the slope of the line may be calculated and used to determine the concentration by dividing the absorbance by the slope. An alternative method of determining concentration from the calibration curve is to mark off the measured absorbance on the ordinate, draw a line perpendicular to the ordinate until it intersects the curve, then drop a perpendicular line to the abscissa from the intersection point. The intersection of the latter line and the abscissa gives the concentration. In practice, only the absorbance and concentration are variables and are in direct proportion, so $A \propto c$, and $A = k'C$ where k' is the slope of the curve A *vs.* c.

Level

Part I of this activity can be used for all levels of students. For basic students, it might be best for you to collect the data with the assistance of several students. For general students, groups of two or three should be able to collect the data for *Part I*, but *Part II* might be better done as a class activity. Honor students should be able to do the entire activity.

Expected Student Background

This activity will probably be the first exposure students have with instrumentation. The experimental procedure is rather straightforward and should not pose great difficulty to students. By this point in the course, students should have the experience with routine laboratory procedures involving the use of glassware, how to clean glassware, and so forth.

Time

Teacher preparation time to mix the 0.020 M $Cr(NO_3)_3$ solution and set out the necessary equipment is about one hour. The spectrophotometers should be checked prior to use. The estimated time for students to perform the activity is 50 min to complete *Part I*. Additional time up to 50 min may be required for *Part II*, particularly if students are required to prepare their own calibration curves.

Safety

Read the *Safety Considerations* in the *Student Version*. Safety goggles should be worn during the activity. The chromium(III) nitrate solution is moderately toxic and should not be poured into the drain. Students are instructed to return the solution actually used in the measurements back into the original container. If there is some possibility that the solution supply will be contaminated, then an alternate disposal procedure should be devised. If it has not been contaminated, the solution may be saved for later use. There are several sources referred to in *SourceBook* that give recommended disposal procedures (see *Safety* section). Local and state regulations must be followed. In view of the disposal problems, only the actual volume of solution needed with a modest excess should be prepared. Caution students to wash their hands with soap and water at the end of the activity.

Materials (For 24 students working in pairs)

Nonconsumables

6 Spectronic 20® spectrophotometers (per class)
24 Small test-tubes (13-mm x 100-mm) or 24 glass cuvettes
12 Plastic wash bottles
Tissue paper (Kimwipes® or equivalent)
Buret, 50-mL
Volumetric flasks, 50-mL and 100-mL (5 of each) or graduated cylinders, 50-mL and 100-mL

Consumables

0.020 M Chromium(III) nitrate solution, 250 mL (2.00 g $Cr(NO_3)_3 \cdot 9H_2O$ per 250 mL solution)
Distilled water
Graph paper

Advance Preparation

You should perform the activity beforehand to be familiar with the procedure. Check the spectrophotometers to be certain they are operating correctly. Allow a 20 min warm-up period prior to use.

To prepare the solution, use 2.00 g $Cr(NO_3)_3$ per 250 mL of solution. Weigh the solute carefully. The unknowns are prepared by successively diluting the 0.020 M solution using 100-mL volumetric flasks to bring the volume $Cr(NO_3)_3$ in Column 3 to final volume (Column 6). Use these solutions to prepare a calibration curve and student unknowns. Use a buret to measure all volumes. Have the 0.020 M $Cr(NO_3)_3$ solution available in several plastic bottles, at least one per spectrophotometer. Make the dilutions according to the following table.

Solution No.	Dilution Factor	mL $Cr(NO_3)_3$	M $Cr(NO_3)_3$ (initial)	M $Cr(NO_3)_3$ (final)	Volume (mL) $Cr(NO_3)_3$
1	1	N/A	0.020	N/A	250
2	2	50	0.020	0.010	100
3	4	50	0.010	0.005	100
4	8	50	0.005	0.0025	100
5	16	50	0.0025	0.0013	100
6	32	50	0.0013	0.00065	100

Figure 1. Dilution data for $Cr(NO_3)_3$.

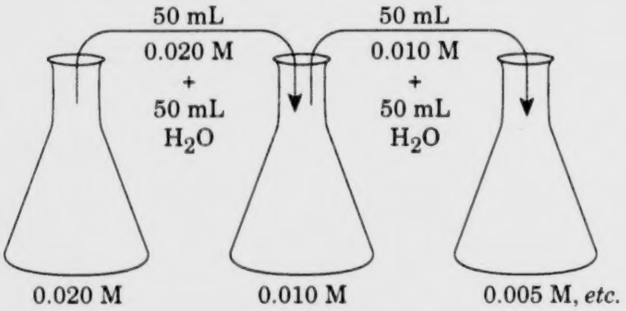


Figure 2. Illustration of dilution process from data in Figure 1.

Pre-Laboratory Discussion

Demonstrate for students the techniques involved with using a spectrophotometer. In particular show them how to clean, fill, and place the test-tubes (or cuvettes) in the instrument. Show them how to set the percent transmittance to 0 and 100%. A transparency master showing a front view of the Spectronic 20® with the controls identified is in the *Appendix*. Show students how to use the calibration curve to determine an unknown concentration.

Students should have little difficulty in preparing a data table. For *Part I* a simple three column table is needed. *Part II* needs a simple table to record the wavelength used, the percent transmittance recorded and the calculated absorbance. If necessary, help students design a data table.

A useful activity for the pre-laboratory portion of the activity is described in *Demonstration 5* in the *Atomic Structure* module. A beveled piece of white chalk is placed in a sample tube in the cell holder of the Spectronic 20. Looking "down the tube" allows one to see the color of the selected light radiation. It is suggested that students view the color every 25-50 nm in the visible range. The monochromator that is part of the Welch ChemAnal® System is another good way to show the colors of light used. Mount the monochromator separately on the optical bench, and use a white piece of paper as a screen to view the colors corresponding with light selected every 25-50 nm wavelength. One advantage of the ChemAnal® monochromator is that the lid swings out of the way so that the "works" inside can be viewed directly while the instrument is being used, removing some of the "black box" aspects of the instrument.

Teacher-Student Interaction

Once students begin the laboratory activity, circulate among them and watch that correct techniques are being used. Pertinent questions may be asked at this time. In particular students need to be aware that the test-tube/cuvette needs proper alignment in the sample holder, that 0 and 100% transmittance needs to be checked during usage at each new wavelength, and that care should be exercised in reading the instrument's meter.

Anticipated Student Results

The following table shows typical data obtained in *Part I* of the activity. The data show one transmittance maximum at 500 nm, thus the graph of the data also show one peak at 500 nm wavelength corresponding to an absorbance minimum. Two absorption maxima at about 415 nm and about 580 nm are present. For *Part II*, the student should measure the absorbance at 580 nm, and then use the calibration curve to measure the unknown concentration to within ±5 % of the accepted value [see Percent Transmittance (%T) to Absorbance (A) Conversions in the *Appendix* for conversions].

Wavelength (nm)	%Transmittance (%T)	A	Wavelength (nm)	%Transmittance (%T)	A
375	64.0	0.194	500	83.0	0.081
400	48.5	0.314	520	72.0	0.143
405	47.0	0.328	530	67.5	0.171
415	46.5	0.333	540	63.0	0.201
425	53.2	0.274	550	58.5	0.233
440	60.0	0.222	570	54.0	0.268
455	71.5	0.146	580	53.0	0.276
470	80.0	0.097	600	56.0	0.252
490	82.5	0.084	625	66.3	0.178

Figure 3. Absorbance vs. wavelength data for 0.020 M $Cr(NO_3)_3$.

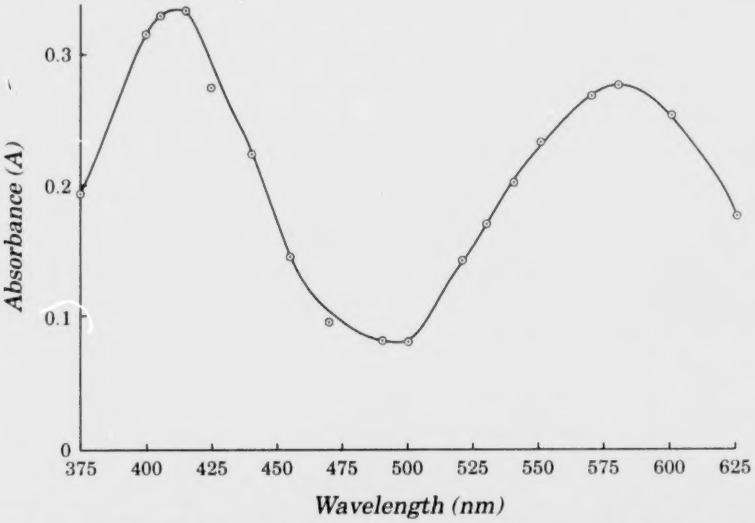


Figure 4. Plot of absorbance vs. wavelength from data in Figure 3.

Answers to Implications and Applications

1. Two absorption maxima appear at the transmittance minima of about 415 nm and 580 nm.
2. The absorption maxima correspond to violet and orange light (400-450 nm and 600-650 nm, respectively).
3. On the basis of the answer to Question 2, a red colored solution would absorb a complementary color. In the case of $Cr(NO_3)_3$ the green color of the solution results because it absorbs its complementary magenta color and transmits green. Thus we expect that a red colored solution would transmit red light.
4. Two uses of an absorption spectrum are to identify an unknown substance and to determine the concentration of a solution of a known substance.
5. A sample substance in solution when placed in the path of light between the monochromator and detector of a spectrophotometer may transmit some, all, or none of light. Light absorption occurs at wavelengths at which the energy of light photons corresponds to the energy needed to excite electrons in atoms, ions, or molecules in the sample.
6. Although the unaided human eye can detect subtle differences in the intensity of colored light, it is difficult to quantitatively measure the differences. Thus, the spectro-photometer is an extension of the sense of sight because it enables the measurement of color intensity to be done routinely and accurately.

Solution Number	Concentration (M)	A
1	0.020	0.333
2	0.010	0.163
3	0.005	0.084
4	0.0025	0.041
5	0.0013	0.019
6	0.00065	0.011
Unknown	0.017	0.256

Figure 5. Calibration data.

Post-Laboratory Discussion

During the post laboratory discussion, help students to graph A *vs.* λ (nm). To measure the concentration of unknowns, absorbance maxima must be known in order to set the correct wavelength for the procedure. It would be useful to students to point out that the concentration of a substance is directly proportional to the area under the peaks in an absorbance spectrum.

For *Part II*, help students use the A *vs.* concentration graph. Have several copies and a transparency of the graph available. Use a hypothetical absorbance and the transparency to show how to read the concentration from the graph. Find the absorbance on the vertical axis and draw a line parallel to the concentration axis beginning at this point until it intersects the graph. Then draw a line from the intersection parallel to the absorbance axis until it intersects the concentration axis. The intersection gives the concentration of the unknown.

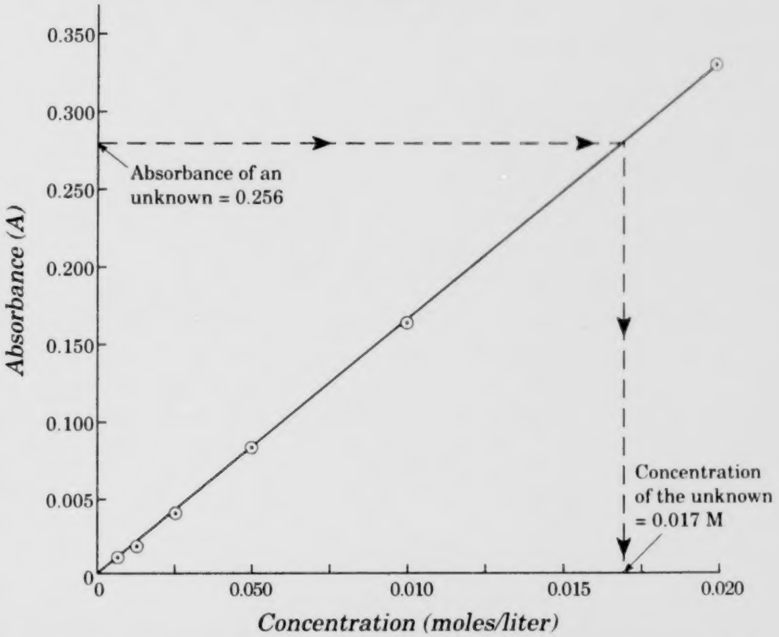


Figure 6. Calibration curve of absorbance* vs. *concentration for $Cr(NO_3)_3$ at 415 nm with example of unknown determination.

Extensions

1. Students can be instructed in how to prepare their own calibration curve for this activity. This preparation would give them practice in quantitative subdilutions and calculation of dilution concentration. Each group of students could be assigned one subdilution, and data could be pooled.
2. Other solutions lend themselves well to this kind of study. The absorbing species in the chromium(III) nitrate solution is $Cr(H_2O)_6^{3+}$ ion. When iron(III) chloride is dissolved in 0.1 M HCl to form a 0.10 M solution, the ion $FeCl_4^-$ is formed. A 0.30 M $Cu(NO_3)_2$ solution that is also 2.0 M in NH_4NO_3 forms the $Cu(NH_3)_4^{2+}$ ion. These solutions can be used for a study similar to the one in this activity.

Assessing Laboratory Learning

1. Laboratory technique may be assessed by noting how the experimentally determined concentration compares with the accepted value of the unknown concentration. Good technique would give a result within ± 1 %. A result within ± 5 % is quite acceptable and might be given a grade of "A." A result within ± 10 % would be a "B," and a result within ± 15 % would be a "C."
2. Use a laboratory practical test to assess instruction. One possible test is to give students a solution of unknown concentration along with a calibration curve and the wavelength to use. Grade on the basis of how closely the student's obtained value compares to the known concentration of the solution.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. Describe the basic principle of molecular spectroscopy. *[See Central Concept 1.]*
2. What energies are involved in molecular spectroscopy? *[Energies from the far ultraviolet through the radiowave region are useful in molecular spectroscopy.]*
3. Describe the principle upon which X-ray diffraction works. *[See the discussion of X-ray diffraction in* Pictures in the Mind *section.]*
4. Describe the principle upon which nuclear magnetic resonance works. *[See the discussion of NMR in* Pictures in the Mind *section.]*
5. Describe the principle upon which mass spectrometry works. *[See the discussion of mass spectrometry in* Pictures in the Mind *section.]*
6. Describe some of the applications of instrumentation. *[Students will probably need to do some library reading to answer this question. They will possibly discuss qualitative and quantitative analysis, quality control,* etc.*]*
7. Describe some uses of instrumentation in your community. *[Student answers will vary. Some possibilities involve water treatment, sewage treatment, medical tests,* etc.*]*

Analogies and Metaphors

Instrumentation is used as an extension of the senses to "see" how atoms and molecules behave.

Using the "black box" activity as a class activity shows inductive reasoning as an analogy to what is done when using instrumentation. The "black box" in this case is a box that contains a single, simple object such as a cylinder, a ring, a cube, and so forth. The object is placed in the box and sealed with tape. The student's task is to build a model in terms of some object whose behavior is well understood as being an explanation of the behavior of the object in the box. The student is allowed any "experiment" that does not damage the box or its contents. (This activity is similar to the Obscertainer Kit activity in the *Atomic Structure* module.)

A systematic way to carry out this activity is to ask a question, design an "experiment" to answer the question, make the observation, and then formulate an assumption on the basis of the observation. For example, the question might be, "Does the object roll or slide?" The "experiment" then would be to carefully tilt the box in various directions while listening carefully. The next step is to record what is heard—either it rolls or slides or it may roll in one direction and slide in the perpendicular direction. The assumption then would be that the object rolls in all directions or rolls in one direction and slides in another, depending upon what is heard. After a series of such steps, the student should be able to describe an object that is a good model of the object in the box. Of course, intrinsic attributes such as color cannot be determined this way; however, using a magnet as an "instrument" would allow the decision about whether the object is magnetically susceptible or not.

CEPUP, Chemical Education for Public Understanding Program, developed by the Lawrence Hall of Science of the University of California at Berkeley, is a modular approach to developing scientific literacy in the general population. Although it is directed toward students in middle/junior high schools, there is an activity in the "Determining Threshold Limits" module that would be a good student activity to illustrate why instrumentation is essential to the chemist. The activity involves diluting food coloring until it is no longer visible to the unaided eye. Then, instrumentation must be used to detect the presence of the coloring material (refer to *Equipment and Instrumentation* for additional information).

The Basic Principle of Spectroscopy

The principle behind all absorption spectroscopic methods—microwave, ultraviolet, visible, infrared, NMR—is the same. It involves resonant absorption of energy by different systems. A good analogy is that of a small boat in water resonating to the frequency of a water wave that is related to the length (or beam width) of the boat. The small boat will rock most violently in response to a wave that is about the length of the boat. The length of the wave is determined by the wave's frequency.

What in a molecule absorbs energy? It depends upon the energy of the quanta being absorbed. Lower energy quanta affect the rotational motion of molecules as a whole. An HCl molecule, for example, will rotate about its center of mass upon absorbing a sufficiently energetic quantum of energy. But just like electronic energy, rotational energy is quantized, that is, there are only certain allowed rotational energy levels. Generally, rotational quanta have frequencies that fall in the microwave region of the electromagnetic spectrum. Molecules can also vibrate either by stretching or bending the bonds. Thus, molecules may absorb energy affecting these motions.

A good analogy for this vibration type is two spherical masses suspended by threads and connected together by springs. Consider two such spheres of equal mass. When connected together by a stiff spring, the masses vibrate at a greater frequency than when connected by a less stiff spring. Similarly, for the same spring, spheres with smaller masses will vibrate at a greater frequency than more massive spheres. The spring stiffness is analogous to the stiffness of a chemical bond.

Pictures in the Mind

How do scientists obtain knowledge of molecular structure details? The following brief descriptions of instrumental techniques, although not exhaustive, give some idea how this information is obtained. These techniques play a large role in developing "pictures in the mind" of molecular structure. Gas chromatography is discussed in *Pictures in the Mind* in the *Separations* module. Specific applications of several instrumental techniques are presented in *Links and Connections* in the *Forensic Chemistry* module.

Infrared Spectroscopy (IR)

"Pictures in the mind" are useful in understanding infrared spectroscopy. When ball-and-spring models are used to represent molecules, the spring is a good model for the behavior of the chemical bond between two atoms. Molecules absorb infrared radiation at wavelengths 1.5×10^4 to 2.5×10^3 nm. These wavelengths correspond to frequencies of 2×10^{13} to 12×10^{13} Hz. An analysis of the energy of the radiation shows that the absorptions are associated with the excitation of vibrational motions. These to and fro motions of atoms at opposite ends of a chemical bond occur at natural frequencies just like the natural frequency of a ball-and-spring model. The masses of the atoms in the molecule, the shape of the molecule, and the strengths of the chemical bonds fix the natural vibrational frequencies.

Knowing the molecular formula and analyzing frequencies, provides information about the molecular moments of inertia, the molecular geometry, and the chemical bonds. Infrared spectroscopy works with gaseous, liquid, and solid compounds. It may also be used to "identify" compounds. The IR spectrum of gaseous HBr and DBr (deuterium bromide with the H in HBr replaced with heavy hydrogen, D) is shown in *Transparency Masters* in the *Appendix* (see *References*, Pimentel, 1963, p. 249.) The only difference between the two spectra is that in DBr, the absorption is shifted to a higher frequency (shorter wavelength) due to the greater mass of the D atom. Otherwise, the absorption patterns are basically the same. More complicated molecules have more detailed spectra, but the spectrum for each molecule is so characteristic that it may be used to detect the presence of the particular substance.

Nuclear Magnetic Resonance Spectroscopy (NMR)

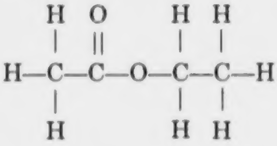
In 1945, Felix Block (Stanford University) and Edward M. Purcell (Harvard University) independently observed an interesting phenomenon concerning the magnetic moments of matter. When a magnetic field is applied to some types of matter, the atomic nuclei in the sample align their spin axes in certain definite orientations. Since that time the significance of Nuclear Magnetic Resonance (NMR) has reached extraordinary proportions. Because of its multiple roles in both chemical and biological sciences, NMR is one of the fastest growing and most widely used instrumental technologies.

Due to the properties of mass and charge, nuclei appear to behave as magnets. These nuclei are also spinning, and the spinning electric charges generate magnetic fields. When an external magnetic field is applied, interaction occurs with the nuclei. Hydrogen is such a nucleus.

There are two possible orientations for a spinning proton (H) in the nucleus of an atom; it may be aligned either with or against the external magnetic field. It is possible to measure the frequency of the electromagnetic radiation (radio waves) required to change the orientation of the proton from one magnetic dipole to another, resulting in a net absorption of energy by the hydrogen nuclei. When the energy absorbance is measured, an NMR spectrum of the sample can be obtained.

Since the magnetic field is held constant during NMR experiments, each nucleus requires a different radio frequency (called a chemical shift) for resonance to occur. Graphically, the x-axis of the NMR spectrum is the frequency difference between the unknown compound and a reference compound. The y-axis corresponds to the relative number of nuclei absorbing energy at a given radiofrequency.

The NMR spectrum in *Transparency Masters* in the *Appendix* was obtained for the compound (ethyl acetate) whose structural formula is shown.



$$\begin{array}{ccccccccccccc} & & H & & O & & & & H & & H & & \\ & & | & & \| & & & & | & & | & & \\ H & - & C & - & C & - & O & - & C & - & C & - & H \\ & & | & & & & & & | & & | & & \\ & & H & & & & & & H & & H & & \end{array}$$

The triplet peak (three-line group) is derived from the CH_3 group on the right of the molecule. The singlet peak is derived from the CH_3 group at the left side of the molecule, and the quartet peak (four-line group) is derived from the CH_2 group near the center of the molecule. If the functional groups present in the molecule are known, then the structure may be determined.

NMR spectroscopy is widely used in medicine. Magnetic Resonance Imaging (MRI) is the term used to describe the application of the principles of NMR spectroscopy to scan internal tissues of living organisms, including human beings. MRI can be done on almost any part of the body. Its applicability depends on the resonance of water molecules, and it can be used to determine the water content of tissue in the body. MRI is a nonintrusive procedure. It does not involve the use of harmful radiation such as X-rays, nor are dyes and pigments needed. MRI, by revealing the chemical composition and the density of tissues within the body, can allow physicians to diagnose any abnormalities that may be present in these tissues.

Perhaps the best application of MRI is for imaging parts of the nervous system. Lesions and tumors of the brain and spinal cord are shown with excellent resolution. MRI is also excellent in studying disorders of the circulatory system, eye, and musculo-skeletal system. One of the interesting facts is that prior to using MRI, it must be definitely established that there are no iron chips or splinters in the subject's eyes. If any iron fragments are present, then grave damage to the eye, even blindness, might occur. This would happen because the very strong magnetic field used with the technique would literally rip the iron fragment out of the eye. Depending upon the size of the fragment, it could simply puncture the eyeball or literally cause it to explode. The disadvantages of MRI are the costs of instrumentation, electrical energy used to run the instrument, and the training of the scientists to use it. MRI promises to be one of the most useful techniques for medicine in the future.

NMR is already an indispensable tool for scientists in chemistry, biology, and medicine. Its importance cannot be overemphasized. Applications of the technique by chemists have revolutionized chemistry. The technique is influencing research fields in biochemistry, materials research, geochemistry, botany, physiology, and medical sciences. Unfortunately, along with the improvement of NMR instrumentation, the cost of the increases in its utility have been almost exponential. In thirty years, the cost of commercial instruments has risen from about $55,000 to about $850,000.

X-ray Diffraction

X-rays have frequencies near 10^{18} Hz and wavelengths near 10^{-1} nm. X-rays can be deflected in regular patterns from parallel planes of a crystal with similar dimensions. The resulting pattern is either photographed or detected electronically. The pattern is determined by the spacing of the atoms or particles in the crystal and their spatial arrangement. X-rays are used since the scattering effects only occur when the wavelengths of the radiation are of similar dimensions to the particle separations within the crystal. The patterns produced are unique to the crystalline material being examined and thus serve as a tool for definitive identification and structure determination. Because of the complexity of X-ray data, the availability of computers has significantly facilitated their analysis.

Mass Spectrometry

In mass spectrometry, a gaseous ion is accelerated to a known kinetic energy by an electrical field. The ion's mass can be measured either by tracking its curved trajectory through a magnetic field or by its time of flight over a fixed distance to the detector. The production of molecular ions causes some fragmentation of molecules and gives a collection of ions. The masses of ions are determined by the structural units in the original molecule. A mass spectrum of $CF_3\text{-}CH_3$ will include a mass peak for the parent ion $(CF_3\text{-}CH_3)^+$ at 84 u. It also includes mass peaks at 15 u and 69 u due to $(CH_3)^+$ and $(CF_3)^+$, respectively. These are logical structural subunits of the parent molecule. Thus, the mass spectrum gives more information than just the molar mass of the original molecule. (Actually, many more mass peaks would be observed due to other fragmentation patterns of the molecule; however, these were not mentioned for the sake of simplicity.)

Mass spectrometers are frequently coupled in tandem with other instruments, to obtain specific information about the components in mixtures. When coupled with a gas chromatograph, the mass spectrometer provides one of the best general purpose analytical instruments available. The combination has application in chemical, biological, geological, environmental, and crime laboratories.

An overhead transparency illustrating the operation of a mass spectrograph is included in the *Appendix*. The transparency shows the separation of neon into its three primary isotopes.

Other

There are other instrumental methods besides those previously discussed. Of particular note are lasers and computers coupled with instrumentation. Synchrotron light sources (X-rays), free-electron lasers, neutron diffraction, electron spin resonance, Raman spectra, electron diffraction, and other instrumental techniques also are widely used in chemical research. The electron and scanning electron microscope also play a role in chemical research. The newest microscope, scanning tunneling microscope (STM), is reported to be able to "see" and "feel" contours of atomic and molecular surfaces.

TIPS FOR THE TEACHER

Language of Chemistry

absorption spectrum plot of absorbance *vs.* wavelength of radiation absorbed for a given substance or mixture.

chromatography technique for separating mixtures using differences in solubility and absorptivity.

emission spectrum dispersion by a prism or diffraction grating of the wavelengths of electromagnetic radiation produced by an emitting source. For example, an atomic emission spectrum consists of those specific wavelengths corresponding to electronic transitions from higher to lower energy levels.

infrared spectroscopy detection and recording of the wavelengths of infrared radiation causing molecular vibrations (that is, vibrations of bonds between atoms) absorbed by molecules and polyatomic ions.

nuclear magnetic resonance spectroscopy measurement of the absorption of energy by nuclei in a strong magnetic field. The energy is supplied by high frequency radio waves.

spectrophotometer instrument that passes electromagnetic radiation through a substance at a given wavelength (or frequency) and measures the amount of radiation absorbed or transmitted.

Pattern Recognition

Infrared spectra provide the means to identify substances by comparing the spectrum of an unknown compound with spectra recorded in atlases of IR spectra. The absorption pattern is characteristic and allows relatively quick identification, as discussed in *Pictures in the Mind*. Similarly, substances can be identified from the NMR spectrum.

Problem Solving

1. The **Beer-Lambert Law** gives students the opportunity to do some simple mathematical calculations involving logarithms. A scientific calculator with a logarithm function greatly simplifies the calculation. The law, as shown in *Part II* of *Activity 1*, is straightforward in the sense that it may be solved in a chain operation using a calculator. The law states:

   $$A = \log_{10} 100 - \log_{10}(\%T) = 2 - \log_{10}(\%T) = k'c$$

   Since the logarithm of 100 = 2, the calculation using a calculator then means entering 2, then a subtraction (–) sign, then (%T), and finally the log button. Pressing the equal (=) button will give the absorbance. *Percent Transmittance (%T) to Absorbance (A) Conversions* table in the *Appendix*, which gives the conversions between %T and absorbance for values from 1%T through 100%T, may be used as a student handout or as a transparency master.

2. **Determining Crystalline and Molecular Structure.** Many naturally occurring substances have physiological activity, and quite a few of them have a beneficial therapeutic effect. Normally, it is difficult, if not impossible, to obtain large amounts of these beneficial compounds from natural sources since they exist only in minute amounts. To synthesize the compound and its close derivative to be used in medication, it is necessary to know the compounds' structures. Thus one reason for undertaking a structure determination is to be able to synthesize a compound of interest.

   One of the problems faced, and solved, is to use modern X-ray diffraction for this purpose coupled with mass spectrometry, and frequently nuclear magnetic resonance. For organic compounds, infrared spectra are also helpful.

   The breakthrough was development of instrumental techniques allowing useful results to be obtained from rather small quantities of substances. It is now possible to determine the crystalline and molecular structures for minute amounts of substances. Armed with this information, chemists may develop schemes for synthesizing the compounds. This was frequently not possible with classical chemical methods of structure determination since not enough of the active compound could be isolated for study.

3. **Other Problem-Solving Instruments.** CAT-scanning and X-ray mammography are other examples of problem solving using instrumentation utilizing X-rays. It must be acknowledged that these techniques, although not primarily chemical in nature, have had a large impact upon the practice of medicine as diagnostic tools. Magnetic Resonance Imaging (MRI), discussed previously, is another such technique. It should be emphasized to students that something that results from basic research frequently is then applied in somewhat surprising ways to solve seemingly unrelated problems.

Decision Making

Instrumentation is used to monitor the environment: acid rain, radon testing, asbestos abatement, ozone depletion, *etc.* Do we place too much reliance on instrumentation? What about biochemical instrumentation? How reliable are automated blood tests? AIDS tests? Breathalyzer tests (see *Chemistry in Medicine* module)? These are some questions that may be assigned to students to research and report back to the class.

In January 1991, the Environmental Protection Agency issued final drinking water standards for 38 contaminants (Ember, 1991, *Chemical and Engineering News*). The total of standards for drinking water now federally enforced is 60. These standards include 17 pesticides, 10 volatile organic compounds, polychlorinated biphenyls (PCBs), eight inorganic compounds, and two substances used to treat drinking water. Although the standards are enforceable by the federal government, states have to administer them. This means that the water supplies in about 80,000 systems nationwide probably will be monitored primarily by instrumentation and/or colorimetric tests that require some treatment, perhaps separations. The monitoring cost is estimated at about $24,000,000 annually, adding from $10 to $800 to consumers' bills for drinking water per year. It is estimated that the rules for pesticides alone will force consideration of pesticide control in land use. This is an example of how monitoring pollutants brings about decisions about their control. Students might be asked to develop a scenario involving a new instrument that could detect PCBs to a level 1000 times lower than our present capability. How might this new instrument affect future regulations regarding PCBs? Is there ever a limit below which we cannot go?

Modern automated instrumental blood tests have been available for some time. One such test checks 27 different and related blood factors from serum glucose to the LDL/HDL ratio (analytes). To do this on a relatively small sample of blood requires a very sophisticated system of separation and instrumental analysis. How reliable is such a system? This question is very important since the results of such tests are used by physicians to prescribe a corrective regimen when an analyte is out of the reference range. Such tests also play a large role in a physician's diagnosis and prognosis. The tests are used extensively for preventive medicine and to detect an abnormality before other symptoms are manifested. Blood testing is now reasonably accessible to most of the country's population wherever doctors are available. Undoubtedly such testing is extremely beneficial to that part of the population willing to pay for it.

Instrumentation and separations are the basis for decision making in many respects, and the trend of reliance on such results will increase as new technology is developed. What kinds of public policies should be developed in light of these capabilities?

HISTORY: ON THE HUMAN SIDE

Before 1920, the determination of the molecular composition and the molecular structure (geometry) of substances was achieved largely through conventional chemical analysis. It is much more difficult to determine the molecular architecture than the molecular composition in this way. The determination of structural characteristics was accomplished by interpreting the reactions of a substance and chemically identifying the resulting fragments. This type of analysis not only requires a relatively large amount of sample, but also results in the destruction of that sample.

Since 1930, much progress has been made in developing instruments that enable chemists to determine composition, molecular mass, and the geometry of molecules. Most instrumental analyses require only small samples (0.1 g or less) and are nondestructive (except for mass spectrometry). This means that the sample may be analyzed several times, using different instruments. Thus, several different characteristics of the sample may be determined. Combining the data from the different sources then will provide a composite picture of the molecule.

Other historical data is given in the *Pictures in the Mind* section.

A Brief Alphabetical List of the History Behind Instrumentation

Aston, F. W. (1877-1945). Developed the mass spectrograph about 1919. Awarded the Nobel Prize in 1922. He showed that neon actually consisted of three isotopes.

Beckman, A. O. (1900-). A pioneer in the field of instrumentation. Founded the Beckman Instrument Co. This company produced the first relatively inexpensive pH meters and the first infrared spectrophotometers.

Bragg, W. H. (1862-1942) and Bragg, W. L. (1890-1971). A father-son team; pioneered work in X-ray diffraction analysis. They jointly developed what is known as Bragg's Law, relating the wavelength of radiant energy with the spacing in a diffraction grating or crystal and the diffraction angle. They jointly were given the Nobel Prize in 1915.

Bunsen, R. (1811-1899) and Kirchhoff, G. (1824-1887). Developed the emission spectroscope.

Crookes, W., Sir. (1832-1919). Developed the Crookes tube, the forerunner of the cathode ray tube that plays an important role in many instruments.

Davisson, C. J. (1881-1958) and Germer, L. H. (1896-). Discovered that electrons would be diffracted by a crystal the same as X-rays. G. P. Thomson (1892-1975), the son of J. J. Thomson, and A. Reid also showed that electrons were diffracted. Davisson and Thomson shared the Nobel Prize in 1937 for this work. The recognition that electrons also had wave-like properties ultimately led to the electron microscope and similar instruments.

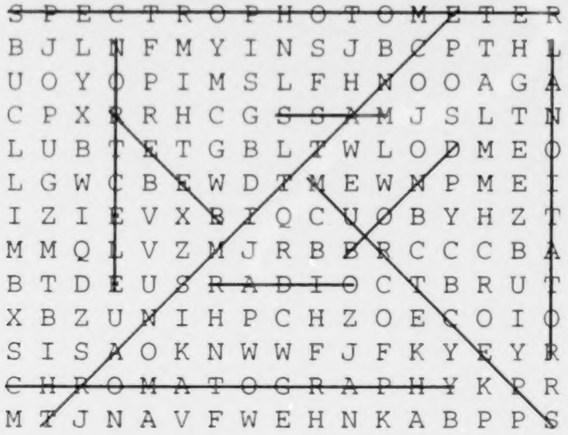
Moseley, H. G. J. (1889-1915). Used X-rays to determine the relationship between the characteristic K lines in an element's X-ray spectrum and the positive nuclear charge of element.

Roentgen, W. (1845-1923). Serendipitously discovered X-rays in 1895 and received the first Nobel Prize in physics for his discovery.

Thomson, J. J. (1856-1940). Discovered the electron in 1897 and positive "rays" in 1913. He suggested that it would be possible to use the rays to analyze chemicals as Aston and others were later able to show.

HUMOR: ON THE FUN SIDE

1. Word Search (see *Appendix* for master copy)



S	P	E	C	T	R	O	P	H	O	T	O	M	E	T	E	R
B	J	L	N	F	M	Y	I	N	S	J	B	C	P	T	H	L
U	O	Y	O	P	I	M	S	L	F	H	N	O	O	A	G	A
C	P	X	R	R	H	C	G	S	S	A	M	J	S	L	T	N
L	U	B	T	E	T	G	B	L	T	W	L	O	D	M	E	O
L	G	W	C	B	E	W	D	T	M	E	W	N	P	M	E	I
I	Z	I	E	V	X	B	I	Q	C	U	O	B	Y	H	Z	T
M	M	Q	L	V	Z	M	J	R	B	B	R	C	C	C	B	A
B	T	D	E	U	S	R	A	D	I	O	C	T	B	R	U	T
X	B	Z	U	N	I	H	P	C	H	Z	O	E	C	O	I	O
S	I	S	A	O	K	N	W	W	F	J	F	K	Y	E	Y	R
C	H	R	O	M	A	T	O	G	R	A	P	H	Y	K	P	R
M	T	J	N	A	V	F	W	E	H	N	K	A	B	P	P	S

1. Energy for nuclear magnetic resonance spectroscopy is supplied by this type of wave.
2. Infrared radiation causes changes in the _____ lengths of molecules.
3. Emission spectra consist of these transitions in molecules.
4. Fraction of incident radiation not absorbed by a solution.
5. Instrument that measures the wavelength and amount of absorption of specific wavelengths when electromagnetic radiation is passed through a substance.
6. Method that separates mixtures based on solubility and absorptivity differences.
7. Range of wavelengths and energies.
8. Type of spectrum that results when molecules are fragmented by an ionizing beam of electrons.
9. A = abc is an algebraic expression of the ____-Lambert Law.
10. Type of spectrum produced by molecular absorption of microwaves.

Answers: 1. RADIO 2. BOND 3. ELECTRON 4. TRANSMITTANCE 5. SPECTROPHOTOMETER 6. CHROMATOGRAPHY 7. SPECTRUM 8. MASS 9. BEER 10. ROTATIONAL

2. See cartoons at end of module.

MEDIA

1. Software published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   a. *Bomb Calorimeter Simulation*, by David J. Olney. Vol. III A, No. 2, for the Apple II computer.

   b. *The Computer-Based Laboratory*, by Daniel Krause. Vol. I A, No. 2, for the Apple II computer.

c. *EPR Spectrum Simulator*, by Miguel A. Martinez-Jimeno, Ernesto Brunet and Carlos Sieiro, Vol. VI B, No. 1, for IBM PS/2, PC-compatible computers.

d. *HPLC – An Instrument Simulator*, by Robert C. Rittenhouse. Vol. I B, No. 2, for IBM PS/2, PC-compatible computers.

e. *Mass Spec Simulation*, by Bruce Armitage. Vol. IV B, No. 2, for IBM PS/2, PC-compatible computers.

f. *NO_2 / N_2O_4 Equilibrium Experiment*, by Teresa Anderson Curtin, Darryl Wahlstrom and James A. McCormick. Vol. IV B, No. 1, for IBM PS/2, PC-compatible computers.

g. *Organic Spectroscopy*, by Richard Hiatt. Vol. II A, No. 2, for the Apple II computer.

h. *Proton NMR Spectrum Simulator*, by Kersey Black. Vol. II C, No. 1, for the Apple Macintosh.

i. *Spec 20*, by Ralph Gable and James McCormick. Vol. IV B, No. 1, for IBM PS/2, PC-compatible computers.

2. Software published by Falcon Software, Box 200, Wentworth, NH 03282; (603) 764-5788.

a. *SpectraBook for Windows and SpectraDeck for Macintosh – An Annotated Collection of IR, NMR, CMR and Mass Spectra*, by Paul F. Schatz. $95 for individual copies.

b. *The Schatz Index for Macintosh* , by Paul F. Schatz. The IR and NMR spectra, physical information, references, synonyms and safety data for 400 organic compounds. $200 for individual copies.

c. IR and NMR Simulators of Macintosh and MS-DOS. These simulators are low-cost and wasy to use; they are no-maintenance simulations of the real instruments. Data sets for 300 compounds are available separately. $95 for individual copies of NMR simulator, $75 for individual copies of IR simulator, $200 for IR data set, $250 for NMR data set.

3. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

a. For the Apple II computer running on ProDOS: AR 1201.

b. For the Apple II computer: AP 1201; Laboratory modules LM 002, LM 003, LM 004, LM 005, LM 006, LM 012, LM 015, LM 016, LM 021 (for the Project SERAPHIM Blocktronic and Thermistor).

c. For IBM PCs and PC-compatibles: PC 4201; Laboratory modules LM 002, LM 003, LM 004, LM 005, LM 006, LM 012, LM 015, LM 016 (for the Project SERAPHIM Blocktronic and Thermistor).

4. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

"Mercury Determination Using A Spectrophotometer – Accuracy and Precision," and "A Generic Spectroscopic Instrument," two chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc I (double sided, 60 min.), Special Issue 3.

5. Films and videocassettes published by Ward's Natural Science Establishment, Inc., 5100 West Henrietta Road, P.O. Box 92912, Rochester, NY 14692-9012; (716) 359-2502; (800) 962-2660; (716) 334-6174 (FAX).

   a. *Crystals and Their Structures* (CHEM Study 16-mm film and/or VHS cassette)

      The film covers the properties of crystals, their well defined diffraction patterns in interactions with X-rays, leading to their description as regular, repeating arrangements of atoms. It includes a ripple tank activity showing the principles and measurements by which crystal structures are determined. Good for above average and honor students. It is especially recommended if it is desired to take the student beyond the material on X-ray diffraction presented in this module.

   b. *Molecular Spectroscopy* (CHEM Study 16-mm film and/or VHS cassette)

      The film presents laboratory activities, molecular models, and animation that shows the infrared light absorption process and its relation to molecular properties. It stresses the concept of natural molecular vibrational frequencies, and how the infrared spectrum is used to identify molecules and determine their structures. Good for the above average and the honor student.

To receive information about subscriptions to *JCE: Software* or a summary of the many software and videodisc issues available, contact: *Journal of Chemical Education: Software*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396; (608) 262-5153; (608) 262-0381 (FAX).

To become a member of Project SERAPHIM or to obtain a copy of the Catalog with over 600 programs of instructional software for chemistry teaching, contact: Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396; (608) 263-2837; (608) 262-0381 (FAX).

EQUIPMENT AND INSTRUMENTATION

Several student spectrophotometers are available. Probably the one used most is the Spectronic 20® manufactured by the Milton Roy Company. It is available with either an analog meter display or with a digital readout. The Spectronic 20® is available from most laboratory equipment suppliers.

Several spectrophotometers designed to use a computer are also available. The Blocktronic uses inexpensive materials and software for an Apple II computer. The plans and software may be obtained from Project SERAPHIM (see address in *Media*).

A GowMac gas chromatograph may be obtained from several suppliers as well as electrophoresis and gel electrophoresis equipment and power supplies.

CEPUP (Chemical Education for Public Understanding Project) materials are available from Addison-Wesley Publishing Company, EMD Fisher Scientific Company, Laboratory Aids, Inc., Science Kit and Boreal Laboratories, and Sargent-Welch Scientific Company (see catalogs published by these companies).

The Optical Transform Kit, available from ICE–Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison WI 53706-1396; (608) 262-3303 (voice) or (608) 262-0381 (FAX).

Links/Connections

WITHIN CHEMISTRY

The topic of instrumentation is linked to different fields of chemistry.

1. Instrumentation is used to determine chemical and physical properties. Spectra provide information about bonding, molecular vibrations and rotations, and electronic energy levels. Spectral information is used to elucidate molecular structure. Instrumentation can also be used for quantitative analysis.
2. Forensic chemistry utilizes instrumentation to a large degree for both substance identification and to determine the concentrations of various substances in the bodies of victims of crime or a person suspected of committing a crime. It is widely used in the investigation of illegal drugs, alcohol, and other life-threatening toxic substances (see *Forensic Chemistry* module).
3. Many industrial, governmental, and private laboratories use instrumentation to test samples for a great number of different substances. These laboratories incorporate instrumentation such as plasma spectrometry, flame emission and flame absorption spectrometry, laser spectrometry, NMR spectrometry, mass spectrometry, and others. Medical labs use CAT-scans and MRI instrumentation extensively. Industrial chemistry uses instrumentation in quality control and monitoring of reaction streams as well as in batch and continuous processes in the manufacture of substances.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

Since the distinction between chemistry and other disciplines, including the arts and social sciences, is rapidly disappearing, the links between chemical uses of instrumentation and uses in other disciplines is rather broad. Medicine, in particular, makes wide use of instrumentation in microbiology, histology, and pharmacology. Art and archaeology use instrumentation in preservation, conservation, restoration, documentation of art treasures, dating techniques, examination of prehistoric objects, *etc.* Virtually every subdiscipline of chemistry, biology, physics, and earth science uses some form of instrumentation.

Extensions

Students may research in the library, the community, and local educational institutions either a specific instrument or the uses of instrumentation. The research may use interviews, field trips, personal or library research. The information thus gained may be presented to the class in the format of a poster session. The presentation could be about 20 min long.

References

Module developed by Royace Aikin and Daniel Kallus, the Texas team.

Braun, R. D. (1987). *Introduction to instrumental analysis.* New York, NY: McGraw-Hill.

This is a recent textbook that gives broad coverage of instrumental methods in chemistry, although some topics are omitted. All of the instrumental methods considered in this module are included. Other textbooks equally good are available.

Ember, L. (1991). EPA issues more tap water rules. *Chemical & Engineering News, 69*(3), 15.

C&EN is an excellent source of current news and reports affecting society in general and chemists and chemistry in particular. It is a source for items of information about science-technology-society interaction and about "breakthroughs" in the understanding of chemistry, yet it is quite readable by students and teachers.

Lippincott, W. T., Gailey, K. D., Meek, D. W., and Whitten, K. W. (1984). *Experimental general chemistry*. Philadelphia, PA: Saunders.

An excellent laboratory manual that may well serve as a general reference for general laboratory procedures and instrumental techniques. The laboratory manual may also be used to select particular parts of experiments to use with high school classes.

Parry, R. W., Bassow, H., and Merrill, P. (1987). *Chemistry: Experimental foundations* (4th Ed.). Englewood Cliffs, NJ: Prentice-Hall.

The only CHEMS-derived text currently published. Very good information, especially how to present chemistry from an experimental point of view. The companion teacher's guide is a must.

Wilbraham, A. C., Staley, D. D., Simpson, C. J., and Matta. M. S. (1987). *Chemistry laboratory manual.* Menlo Park, CA: Addison-Wesley.

A good, solid high school chemistry laboratory manual, although in a somewhat cookbook style. It presents useful experiments including a good presentation of laboratory safety and laboratory techniques.

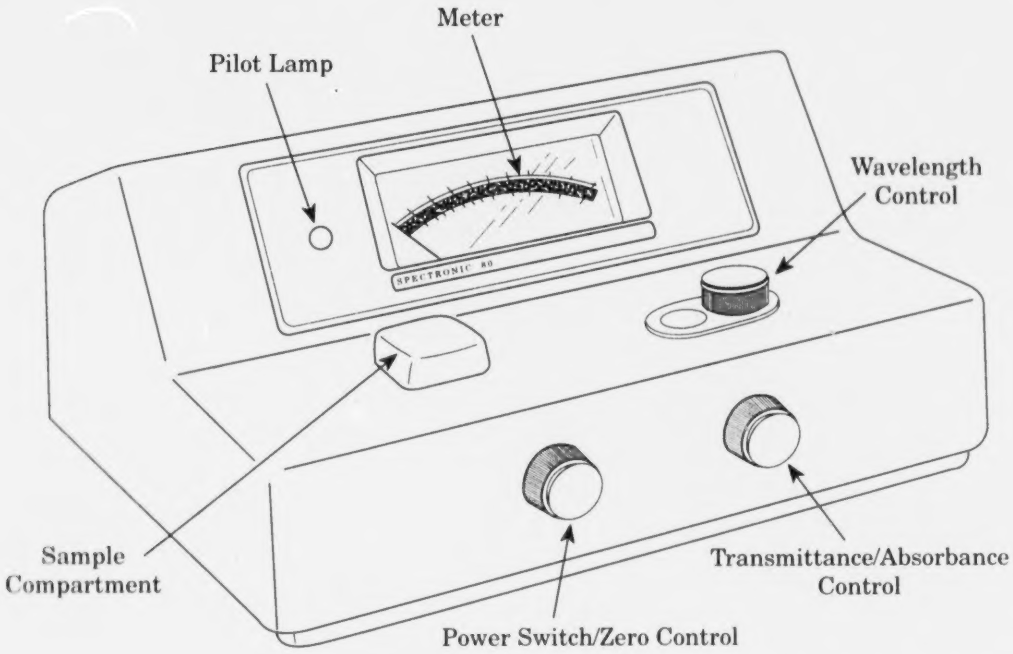
Willard, H. H., Merritt, L. L., Jr., Dean, J. A., and Settle., F. A., Jr. (1988). *Instrumental methods of analysis* (7th Ed.). Belmont, CA: Wadsworth.

A basic text in instrumental analysis that doubles as an excellent reference in this subject.

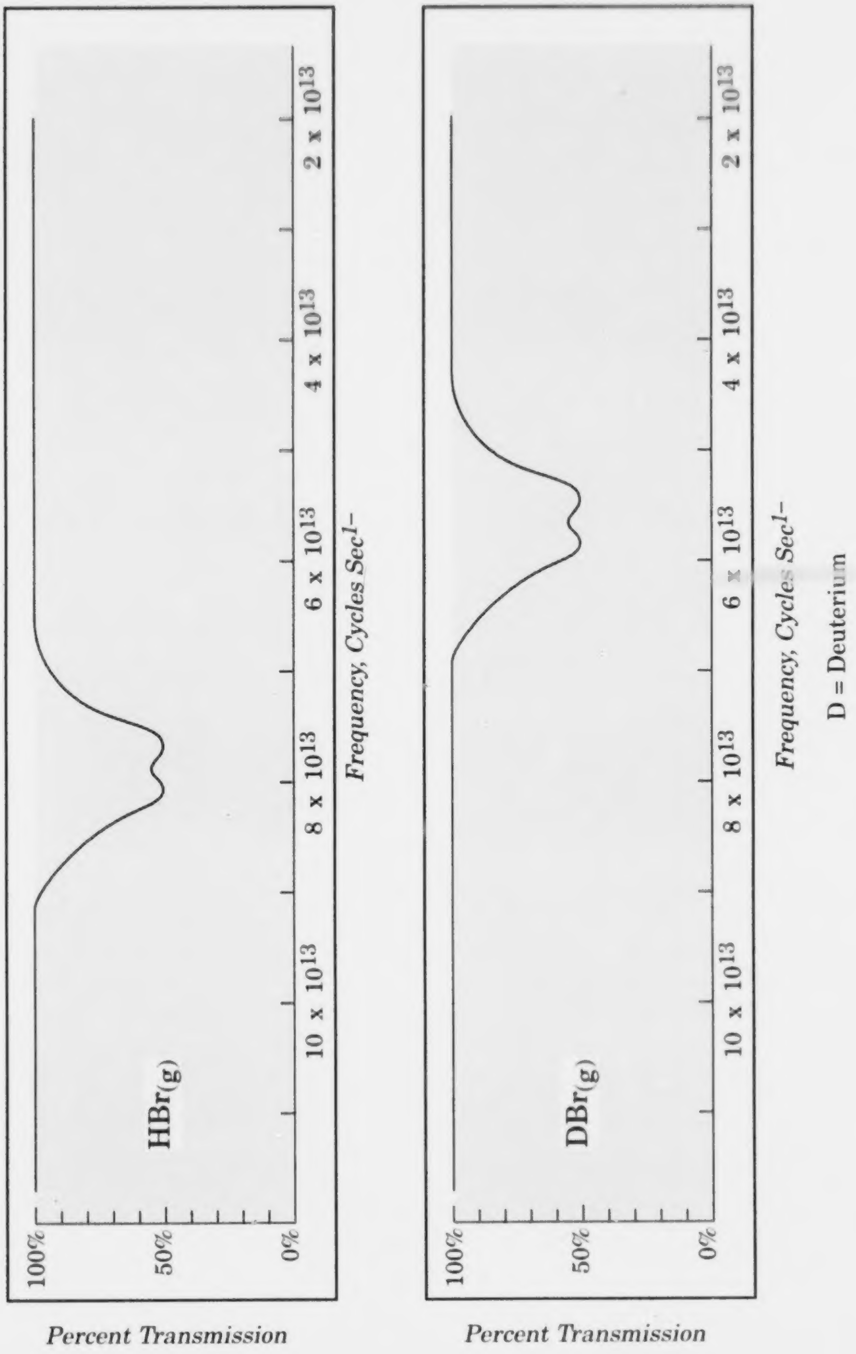
Appendix

- **Transparency Masters**
    1. Spectronic 20® Spectrophotometer showing the controls and their functions.
    2. The Infrared Absorption Spectra for HBr(g) and DBr(g). The spectra show that the heavier DBr(g) absorbs strongly at a lower frequency (longer wavelength) than HBr(g).
    3. Nuclear Magnetic Resonance Spectrum of Ethyl Acetate
    4. A mass spectrograph showing the essential features of the instrument and the separation of neon into its three naturally occurring isotopes, ^{20}Ne (90.92%), ^{21}Ne (0.26%), and ^{22}Ne (8.82%)
    5. Percent Transmittance-Absorbance Conversions
    6. Molecular Motions and Relative Spacing of Molecular Energy Levels (in kilojoules/mol of molecules) Associated with Absorption of Radiation
    7. Word Search
- **Humor**

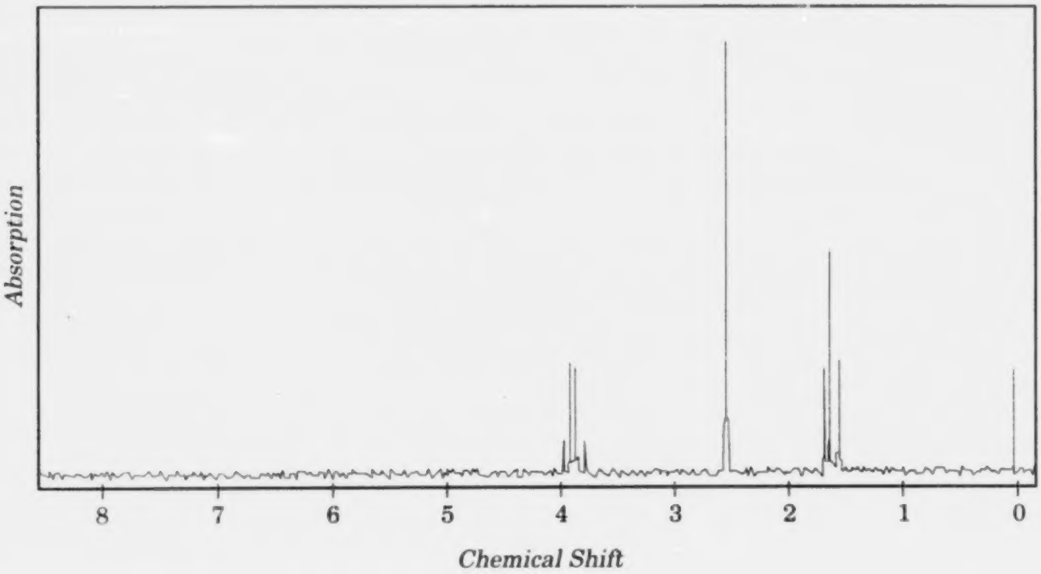
Spectronic 20® Spectrophotometer



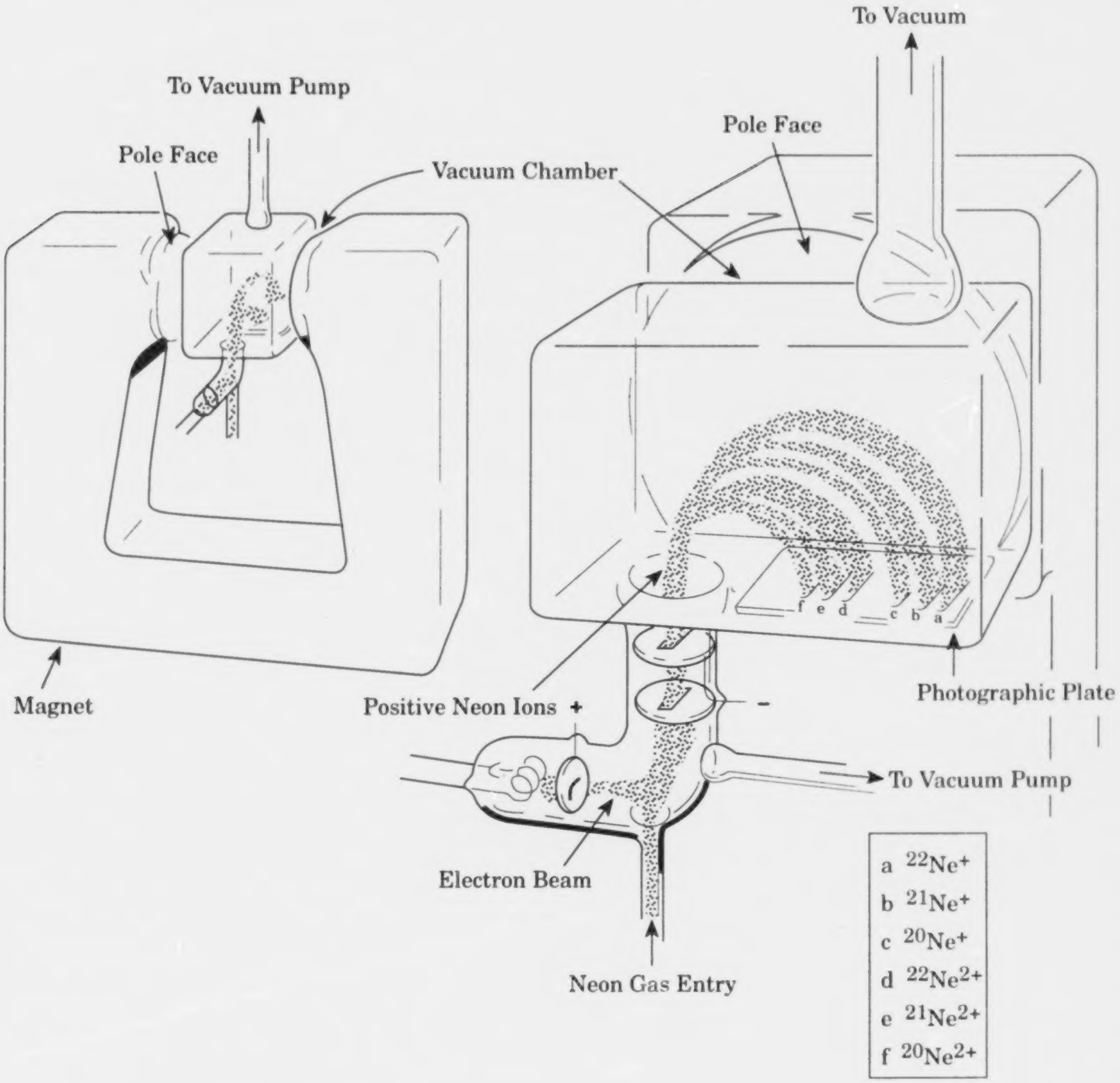
Infrared Absorption Spectra



Nuclear Magnetic Resonance Spectrum of Ethyl Acetate



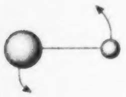
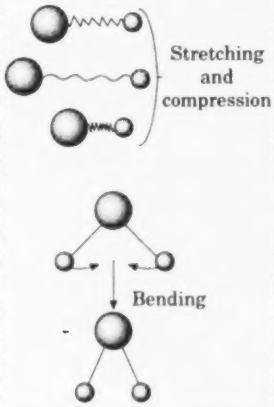
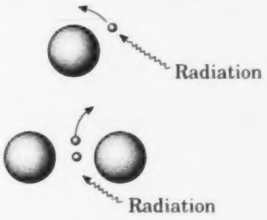
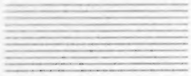
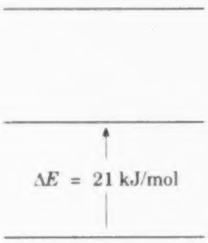
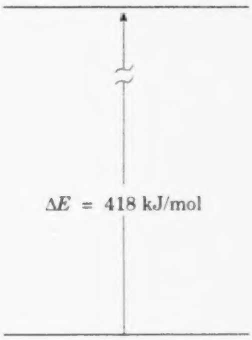
A Mass Spectrograph



Percent Transmittance (%T) to Absorbance (A) Conversions

%T	A	%T	A	%T	A	%T	A
1	2.000	26	0.585	51	0.292	76	0.119
2	1.699	27	0.569	52	0.284	77	0.114
3	1.523	28	0.553	53	0.276	78	0.108
4	1.398	29	0.538	54	0.268	79	0.102
5	1.301	30	0.523	55	0.260	80	0.097
6	1.222	31	0.509	56	0.252	81	0.092
7	1.155	32	0.495	57	0.244	82	0.086
8	1.097	33	0.481	58	0.237	83	0.081
9	1.046	34	0.469	59	0.229	84	0.076
10	1.000	35	0.456	60	0.222	85	0.071
11	0.959	36	0.444	61	0.215	86	0.066
12	0.921	37	0.432	62	0.208	87	0.060
13	0.886	38	0.420	63	0.201	88	0.056
14	0.854	39	0.409	64	0.194	89	0.051
15	0.824	40	0.398	65	0.187	90	0.046
16	0.796	41	0.387	66	0.180	91	0.041
17	0.770	42	0.377	67	0.174	92	0.036
18	0.745	43	0.367	68	0.167	93	0.032
19	0.721	44	0.357	69	0.161	94	0.027
20	0.699	45	0.347	70	0.155	95	0.022
21	0.678	46	0.337	71	0.149	96	0.018
22	0.658	47	0.328	72	0.143	97	0.013
23	0.638	48	0.319	73	0.137	98	0.009
24	0.620	49	0.310	74	0.131	99	0.004
25	0.602	50	0.301	75	0.125	100	0.000

Molecular Motions and Relative Spacing of Molecular Energy Levels Associated with Absorption of Radiation

Radiation Absorbed	Microwave	Infrared	Visible	Ultraviolet
Motion	Rotation	Vibration	Electron transitions	
				
Relative energy level spacings	ΔE = 0.04 kJ/mol 			

Word Search

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S P E C T R O P H O T O M E T E R
B J L N F M Y I N S J B C P T H L
U O Y O P I M S L F H N O O A G A
C P X R R H C G S S A M J S L T N
L U B T E T G B L T W L O D M E O
L G W C B E W D T M E W N P M E I
I Z I E V X B I Q C U O B Y H Z T
M M Q L V Z M J R B B R C C C B A
B T D E U S R A D I O C T B R U T
X B Z U N I H P C H Z O E C O I O
S I S A O K N W W F J F K Y E Y R
C H R O M A T O G R A P H Y K P R
M T J N A V F W E H N K A B P P S
```

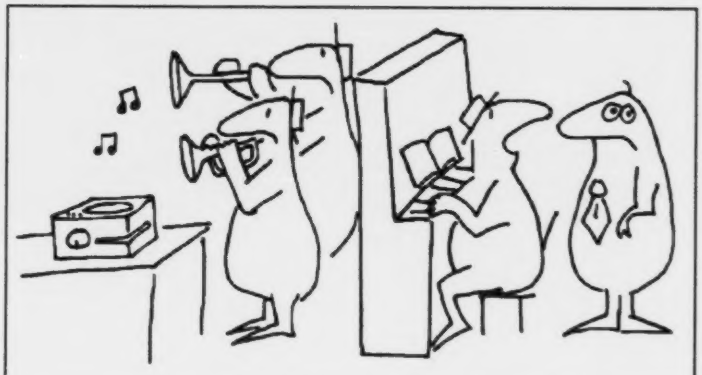
1. Energy for nuclear magnetic resonance spectroscopy is supplied by this type of wave.
2. Infrared radiation causes changes in the _____ lengths of molecules.
3. Emission spectra consist of these transitions in molecules.
4. Fraction of incident radiation not absorbed by a solution.
5. Instrument that measures the wavelength and amount of absorption of specific wavelengths when electromagnetic radiation is passed through a substance.
6. Method that separates mixtures based on solubility and absorptivity differences.
7. Range of wavelengths and energies.
8. Type of spectrum that results when molecules are fragmented by an ionizing beam of electrons.
9. A = abc is an algebraic expression of the ____-Lambert Law.
10. Type of spectrum produced by molecular absorption of microwaves.

Correct me if I'm wrong, but I get the impression that some Ph.D. took a crack at repairing this highly sophisticated machine...

CHEMTECH, June 1980, p. 371. © American Chemical Society. Reprinted with permission.

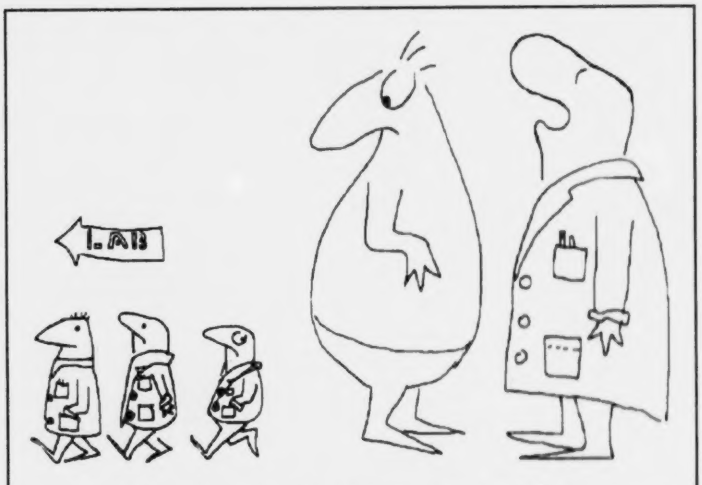
"Test-tube! . . . .What's a test-tube?"

CHEMTECH, January 1980, p. 4. © American Chemical Society. Reprinted with permission.



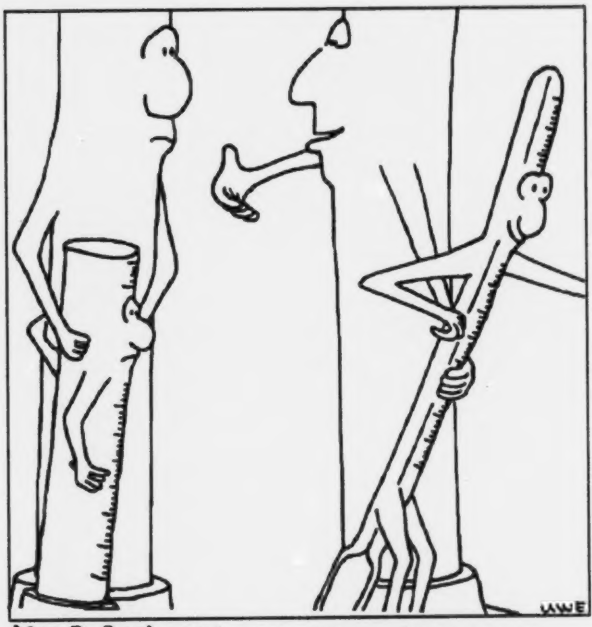
"It was our agent's idea. We have to use a colorimeter to make sure our blues are up to par."

CHEM 13 NEWS, October 1977, p. 1236. Reprinted with permission.



"Yes, we have a small clinical lab. And don't think it was easy finding qualified personnel."

CHEM 13 NEWS, September 1978, p. 30. Reprinted with permission.



YOUR SON MAY JUST HAVE GRADUATED BUT MINE HAS 25 DEGREES ALREADY !!

CHEM 13 NEWS, February 1980, p. 7. Reprinted with permission.

MATERIALS SCIENCE:
CERAMICS & GLASSES

A SourceBook Module

Version 2.0 1994

Funded in part under
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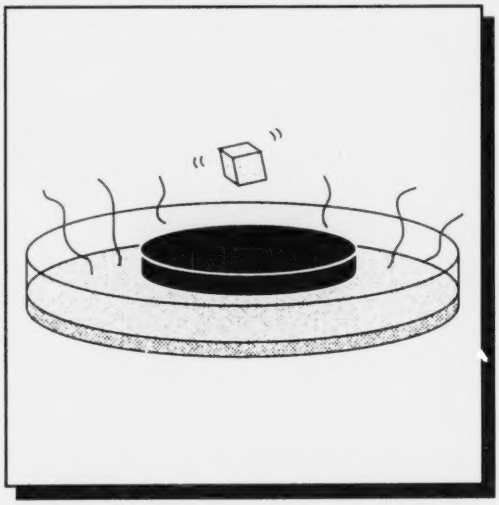


ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

Materials science is a most vital area of modern science and engineering. High temperature superconductors, the coating on stealth aircraft, diamond thin films, semi-conducting computer and solar photovoltaic components are all products of materials science. Metals, plastics, ceramics, glasses, and concretes that go into nearly everything in the construction environment are equally important. Concepts central to understanding materials science are bonding in the solid state and the influence of bonding on such important properties as thermal and electrical conductivity, strength, light transmission, resistance to various chemical and physical environments, and creation of and/or response to magnetic fields. Materials science exists at the interface of chemistry, physics, and engineering and can be studied at every level from descriptive chemistry to theoretical quantum mechanics.

A ceramic is an inorganic material processed or consolidated at high temperatures. Although some scientists claim ceramics are crystalline materials, most ceramists include both crystalline and amorphous materials as ceramics; therefore, glasses are usually considered as a subset of ceramics. Ceramics include a wide range of compounds including silicates, oxides, carbides, nitrides, sulfides, and borides. Although most ceramics contain metal ions, some of them, *e.g.*, silicon carbide, do not.

Ceramics are prepared differently from methods normally encountered in a study of reactions in solution or liquid mixtures. Production of ceramics involves mixing components, shaping, and heat processing. The traditional method of mixing is to grind powders together. An advantage of this method is that it is easy and cheap. The main disadvantage is poor quality control of both particle size and precise chemical composition. The powder mixture is then typically pressed into shape, and sintered to produce the final crystalline product. Sintering is a process of heating at high temperature, but below the melting points of the various components. This process causes binding between powder grains and decreases the size of the spaces between grains. Another method of preparing ceramics uses chemical mixing. This process involves precipitating the particles simultaneously, allowing precise control of both stoichiometry and particle size. This process is more expensive but allows production of more complex materials with superior quality control. Either process forms crystalline ceramics. For glasses, the mixture is typically melted and poured into molds, flattened into sheets, or drawn into fibers.

Ceramics are usually considered covalent network solids, although some of the metal-nonmetal bonds may be ionic. Their chemical reactivity depends on the particular bonds involved, especially bonds at the surface of the material. Their electrical and optical properties depend on the distribution of electrons (see Band Gap Theory in *Links and Connections within Chemistry*). Magnetic properties depend on the spatial distribution of electrons and atomic kernels. Thermal properties depend on these factors and on the masses of the nuclei. There are several ways to think about strength, including wear resistance, toughness, and resistance to shattering. These properties depend more on number and nature of dislocation and grain boundaries than on features related to bonding.

Much about ceramics is poorly understood. The properties of the new class of high temperature superconductors were not predicted from theory, for example, and many of the recent advances in that area have come from educated guesses based on periodic properties of the elements. Many of the professional opportunities for chemists into the twenty-first century will be in the field of materials science.

PLACE IN THE CURRICULUM

Materials Science includes applications of solid-state materials that can be used as an extension to topics on metals and semi-metals or amorphous and crystalline solids. This module would be appropriate to use at the end of the year.

CENTRAL CONCEPTS

1. Materials Science is a subtopic of solid-state matter.
2. Solids can include descriptions of physical and chemical properties such as electrical conductivity, ductility, brittleness, *etc.*
3. Materials can be classified as:
   a. Metals, Semi-Metals, Nonmetals
   b. Glasses and Ceramics
   c. Crystalline and Amorphous
   d. Conductors, Semiconductors, Insulators, Superconductors
4. The focus is on technological applications of materials science.
5. Concepts like band gap energy can be explored to explain conductivity.
6. The topic of nonstoichiometry of inorganic solids can be explored.

RELATED CONCEPTS

1. Electrical energy
2. Energy levels and valence
3. Magnetism
4. Physical properties of solids
5. Stoichiometry
6. Intermolecular force
7. Periodic properties
8. Covalent network, ionic, and metallic bonding in solids
9. Packing of crystals

RELATED SKILLS

1. Stoichiometry calculations
2. Laboratory skills:
   a. Basic manipulation of glassware and chemicals
   b. Operation of an analytical balance
   c. Using a high-temperature oven

PERFORMANCE OBJECTIVES

After completing their study of materials science, students should be able to:

1. describe differences between the microscopic and macroscopic structure of materials.
2. classify everyday materials. (Consider the classroom or a room in a house and attempt to classify all the materials in it by first identifying the material as organic or inorganic, then crystalline or amorphous. Next, the materials should be classified as metals, polymers, ceramics, or glasses. Then the major chemical constituents in the material (elements, compounds or ions present) should be identified, and finally guesses should be formulated regarding how the material was fabricated into its final form.)

3. relate properties of materials to chemical bonding and crystal structure.
4. explain how properties of materials can be altered by changing their chemical makeup or by combining them in various ways with other materials.
5. define specific terminology: sintering, crystalline, amorphous, superconductivity.
6. compare solid state reactions and solution reactions.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Preparation of Colored Glass

Introduction

Glass is an amorphous solid typically made of silica (SiO_2), soda ash (a mixture of sodium oxide, Na_2O, and sodium carbonate, Na_2CO_3), and limestone (calcium carbonate, $CaCO_3$), with small quantities of other materials that affect color and physical and chemical properties. Silica has a very high melting point, and soda ash and limestone are added to cause melting point lowering. These melting point lowering materials are called *fluxes*.

Scientists sometimes describe glass as a supercooled liquid because it is **amorphous** (without regular crystalline form), **isomorphic** (refracts light at the same angle in all directions), and will flow under pressure. Unlike crystalline solids, glasses do not have sharp melting points. This melting point range can be explained by considering the energy needed to break solid state bonds. Crystals are regularly repeating structures, so their bonds have the same energy and they all break at about the same energy input, or temperature. But glasses have bonds going in random directions with differing amounts of stress and strain; hence, these bonds require different energies for breaking and therefore do not all break at the same temperature.

The compounds substituted for soda ash and limestone, and added as trace compounds, determine the properties of a particular kind of glass. Glass fluxed with soda ash and limestone is **crown glass**, and glass fluxed with lead carbonates and oxides is called **flint glass**. If borax, or boron oxide is added to the flux, a **borosilicate glass** is made. Such glass can withstand rapid temperature changes without shattering like flint or crown glass, and is sold under such trademarks as Pyrex™ and Kimax™. You will be making a borosilicate glass in this activity.

Transition metal (*d*-block) trace elements added to glass can cause the glass to be colored. For example, compounds of gold added to the flux produce red glass; cobalt compounds produce blue glass. (You may have used "cobalt glass" in the flame test for potassium.) In this laboratory, you will experiment with adding small quantities of *d*-block metal oxides and carbonates to glass you prepare. The purpose of the activity is to determine **empirically** (*i.e.*, by trial and error) what colors are produced by which *d*-block elements.

Purpose

To use common earth materials to make a consumer and industrial product.

Safety

1. Wear protective goggles and dust mask throughout the laboratory activity.
2. Since rapidly cooling glass sometimes shatters, you may also want to wear some jeans and a long sleeved shirt to protect your arms and legs during this activity.
3. Metal oxides are generally basic; sodium oxide is quite basic—strong enough to hydrolyze your skin and hair if it gets on you. You should likewise not breathe the dusts of these compounds, so be sure to use a dust mask.

4. Glass can *be* hot without *looking* hot. When you prepare a sample of glass, allow plenty of time for it to cool before picking it up. Even then, hold your hand close to the sample to feel any heat coming off. If it doesn't feel too hot when your hand is close to the sample, lightly and quickly touch the sample to feel how hot it is. Only if it feels cool should you pick it up.

Procedure

1. Make sure the furnace is preheated to 1050 °C.
2. A typical recipe for glass mixes one mole sodium oxide, Na_2O, one mole borax, $Na_2B_4O_7$, and two moles silicon dioxide or sand, SiO_2. Calculate the masses for each of these components in grams and determine, by adding them together, the total mass of the glass this would make. Then calculate the mass of each component that would be required to make 10 g glass using the same recipe.
3. After you have weighed the constituents of the mixture, add them to a mortar along with a few crystals (or a little pinch of powder) of the transition metal oxide or carbonate you plan to use as a coloring agent. The more metal oxide or carbonate used, the deeper the color. Grind these materials together in a mortar with a pestle. The result should be a uniform mixture.
4. Put about 2/3 of your mixture in a clean crucible and about 1/3 in a clean dry test-tube for future reference. Make sure you record the compounds and approximate amounts you use. You will be sharing your recipe and your colored glass with your classmates at the end of this activity.
5. Using heat resistant gloves and crucible tongs, slide the crucible into the preheated furnace. If the furnace is too hot to stand in front of, you should get your laboratory partner to hold a heat shield made of sheet metal between you and the furnace door while you slide in the crucible. This should be done quickly, as the metal shield will heat up.
6. Allow your glass to melt for about 20 min. It should have the viscosity (pourability) of warm honey after this time. If it does not, turn the oven up a little and wait 10-20 min longer. (You may have to wait until the next day if the furnace is too cold.)
7. When your sample has melted to the consistency of warm honey, take it out of the furnace using the gloves and crucible tongs, and stir it with a stainless steel spatula to ensure that it is a homogeneous mixture. Once it is homogeneous, put it back in the oven to heat and melt for a few more minutes.
8. Take your homogeneous melted sample from the furnace and pour it as a puddle onto the metal plate provided for that purpose. When it has cooled just enough so that a slight tap with the spatula no longer dents it, slide it into a small metal pan and *put a piece of wire gauze over the pan.* (This is to protect you from flying glass when it shatters from the stress of contraction upon rapid cooling.)
9. When your glass has cooled, show it to classmates. If it has shattered on cooling, put the shards in a test-tube and observe the difference in appearance between the original mixture of powders and this new material called glass. From observing the colors produced by the class, fill out a chart that matches color with additive.
10. Thoroughly wash your hands before leaving the laboratory.

Implications and Applications

1. Observe the samples of oxide and/or carbonate coloring materials along with other compounds of the same transition metal ions. How do the compound colors compare with the glasses that were prepared by you and your classmates?
2. Sometimes the original trace metal ion is oxidized or reduced in reacting with the other constituents used to make the glass. If you noticed any inconsistencies in Question 1 between glass color and compound colors, try to resolve them by comparing the glass color to compounds of other oxidation states of the same transition metal ion.
3. Propose several mixtures that give colors not prepared by the class in this laboratory. Explain why you think this mixture will work, referring to the nature of colors produced by mixing and subtracting light of different colors, and to colors of compounds you propose as additives.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Preparation of Colored Glass

Major Chemical Concept

The major concept of this laboratory activity is the difference between arrangements of atoms in *crystals* and arrangements of atoms in *glasses*. To support the introduction, have students build models of quartz, mica, and asbestos (regular arrangements for SiO_2), and glass in which the Si and O atoms go randomly in every direction, with strands of bonded atoms looping past and among each other in random fashion.

Level

General and honor students.

Expected Student Background

Required background includes stoichiometry, periodic properties, and electron structure of atoms. Understanding will be increased if students have also studied *d*-block elements, their compounds, and the influence of chemical surroundings on energy differences between outer shell orbitals of *d*-block ions.

Time

If students are efficient and the furnace setting is correct, students can finish in 40-45 min. Students should mix their glass powder during one period and store it in a test-tube or other container overnight. Then they will have time for mistakes and for showing each other their glass samples during a the next class period. Students who work slowly may not be able to show their glass until the third day, after it has cooled and/or been stored overnight. To do this activity properly, you should devote three full periods to it. Your faster laboratory students can make models of network solids from styrofoam balls and toothpicks or pipe cleaners while they wait for the rest to catch up. Don't rush anyone; rushing is an invitation for serious burns.

Safety

Read the *Safety Considerations* in the *Student Version*. Encourage students to take time and be careful. The furnace and glass are *hot*. Be sure you have a first aid kit with burn ointment handy. Immediate treatment with cold water is the best first aid for burns.

Materials (For 24 students working in pairs)

Nonconsumables

24 Dust masks
12 Crucible tongs
12 Stainless steel spatulas
12 Ceramic crucibles
12 Mortar and pestles
Balance (precision of 0.01 g or better)
Furnace (any furnace used for firing pottery will work well)
Thick metal plate to be used to pour glass sample onto (stainless steel is best but iron, copper, or zinc plates are satisfactory)
Small metal pan
Wire gauze
Heat resistant gloves
Sheet metal, 1/2 m^2 to be used as a heat shield

Consumables

- Clean sand, SiO_2, 250 g
- Sodium oxide, Na_2O, 250 g (Alfa Research Chemicals, Telephone: 1-800-343-0660)
- Borax, $Na_2B_4O_7$, 300 g
- Numerous *d*-block oxides and carbonates in small quantities. (Avoid *d*-block elements such as mercury, cadmium, osmium, *etc.*, known to be toxic. Refer to the MSDS sheet for the compound's toxicity.)
- Examples of other compounds (nitrates, acetates, sulfates) formed by those same *d*-block metals.

Advance Preparation

Make sure all materials are available for the activity. Of special note is the metal plate upon which students will pour their melted glass and the small pans, screens or wire gauzes they will use for the final cooling. This is to protect students from glass shards generated by shattering when the glass is rapidly cooled. Also, you will save time if you ensure that the furnace is at the proper temperature by testing it with a batch of your own glass powder prior to student use. Once you have the proper setting, leave the furnace on.

Pre-Laboratory Discussion

How you conduct the pre-laboratory depends on the objectives selected. An approach that promotes critical thinking skills is to ask students to hypothesize the colors various additives will produce based on a comparison with the color of compounds of metal ions used as additives. Because the colors of *d*-block element compounds are not consistent, even with the same oxidation numbers, attempting to predict glass color should generate some discussion of the theoretical basis of compound color if students have had that background. Once students have discussed their predictions and reached consensus with regard to colors produced by the additives, they are prepared to test their hypotheses. If you have only a few *d*-block oxides and/or carbonates available, you might also choose to have students predict colors produced by mixtures; use appropriate questioning techniques to make sure they consider the possibility that the additives might react with each other in a redox reaction. Once students have made predictions, use whatever method you wish to assign additives to groups to ensure all available additives (and combinations of additives) are tested. Be sure to record the predictions for use during the post-laboratory discussion.

If you choose to lecture on this topic, you should review the nature of bonding in solids, comparing the organization of ionic and network covalent crystalline solids with the disorder of glasses. Follow this with a review of the relationships between compound color and electron structure as applied to the influence of trace elements on color in glass. Refer to the chart for typical colors produced by small amounts of metal compounds added to the flux.

Compound or Metal Ion	Color
Gold	Red
Selenium	Red
Copper(II)	Blue
Cobalt	Blue
Iron(II)	Green
Iron(III)	Brown
Manganese(IV) Oxide	Purple
Permanganate	Purple
Iron(II) + Manganese(IV) (or Selenium Oxide)	Grey (Colorless)

Teacher-Student Interaction

During the activity enforce safety and good laboratory procedure. As you circulate throughout the laboratory, ask each group which additive(s) they are testing and what color they believe will result.

Anticipated Student Results

Students produce glass samples of various colors (see *Pre-Laboratory Discussion*).

Answers to Implications and Applications

1. This observation depends on what compounds are available for the laboratory. Check for accuracy.
2. Again, this depends on compounds used as additives. Sometimes iron(II) oxidizes to iron(III), creating brown glass with a green additive. Sometimes pink cobalt(II) additives produce blue cobalt glass by changing the chemical environment around cobalt to make tetrahedral cobalt complexes.
3. This is an open question. Make sure students base their predictions on observed properties of additives, colors of other oxidation states, *etc.*, using chemical reasoning instead of guessing.

Post-Laboratory Discussion

Compare predictions with results and ask students to explain any discrepancies. Reasonable explanations include changes in the glass as compared with the additive compound in the chemical environment around the metal ion. This results in a change in the energy difference between electron orbitals. Changes in the oxidation states of additives also result in different species with different absorption characteristics.

Extensions

Many extensions are possible. If you have not studied glass blowing and bending earlier in the year, you can use this as an opportunity for students to practice working with glass. In addition to glass bends and pipets that students typically make, the following projects are also possible with good burners and "regular" sodium silicate (not borosilicate) hollow and solid glass tubing and test-tubes.

SAFETY NOTE: The same safety rules given in the Student Version *of the activity should be used for the extensions.*

1. **Blow a Colored Glass Bubble**

   Have students use the furnace to melt the colored glass they made. As soon as the glass begins to melt (more viscous than warm honey—see Steps 6 and 7 in *Student Version*), light the burner and begin to soften the end of a clean hollow glass tube. (Students will blow on either the tube end itself, or on a piece of rubber tubing attached to the tube end, so cleanliness is the key here. If cleanliness is in doubt, use glass and rubber tubing of a size that enables you to put an individually wrapped disposable drinking straw into the end of the rubber tube to be blown on by the student.) Transfer the crucible of melted glass to a hot pad on the desk top. Place the premelted end of the glass tube (complete with rubber tube and straw if necessary for blowing) into the melted colored glass and twirl it around to pick up a glob of colored melted glass. Blow up the glass glob like a balloon. While the student blows, the glass blob should be over some heat resistant surface, such as ceramic tile. If the glass ball is blown too thin, it will be very fragile; students should also rig up some sort of apparatus with a ring stand and clamps to hang the glass bubble until it cools. With a bit of practice, students can make nearly round hollow colored glass balls from their previously synthesized colored glass. Invite students to bring in tissue paper and small boxes to protect their colored bubbles when taken home. (Although the tube is long enough that there is no danger if a student accidentally inhales, you may wish to caution students to only exhale while glass-blowing. Alternatively, try substituting a fireplace bellows for the source of air.)

2. **Make a Test-tube with a Sidearm**

   A trickier project is to add a glass tube sidearm to a test-tube. First, you must blow a small hole in a large test-tube, about 3-4 cm from the top. To do this, first make a "blower" from a 1-hole stopper that fits the test-tube, a short piece of glass tubing, a long piece of flexible rubber tubing, and a drinking straw to fit the rubber tubing.

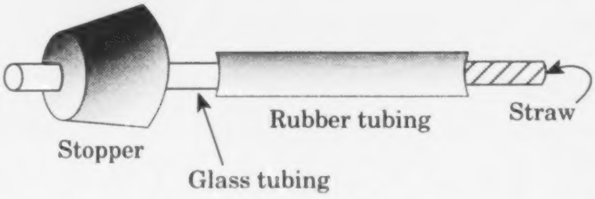


Figure 1. Glass-blowing assembly.

   Place this assembly in the test-tube (about 3-4 cm from the top). Heat a very small spot on the test-tube with a burner to as high a temperature as possible until the spot gets soft. Meanwhile, a student partner can be softening the end of a hollow glass tube. When a soft spot in the test-tube has formed, blow suddenly through the straw to forcefully pop a small hole in the side of the test-tube. Keeping the test-tube in the flame, so the edges of the recently popped hole stay soft, stick the soft end of the glass tube to the soft side of the test-tube so that the glass tube goes over the previously blown hole. Take the assembly out and let it cool. The trick is to stick the test-tube and glass tube together so that the joint doesn't leak. This takes some practice. The connection should be smooth, not lumpy, or it will crack.

3. **Working with a Solid Glass Rod**

   If you can have two different diameters of solid glass tubing for students, they can make a number of interesting art objects. For example, using a larger tube (diameter of 0.8-1 cm), you can make a swan. First, soften the glass in the middle of the tube and push it in to "fatten" the swan body. Second, behind this "fattened" part, heat the tube as hot as possible in a narrow band and quickly pull the tube apart, pulling one part of the tube at a right angle to the other, creating the "tail". When this has cooled, soften the tube on the other side of the fattened body along several cm of tube. Pull that part more slowly, bending it into a swan's neck-shape. Make sure that the neck and the tail tip both point in the same direction. When that has cooled, intensely heat the end of the neck and pull it out into the swan's beak. Finally, intensely heat the end of a small diameter glass tubing and "paint" the wings onto the previously prepared swan. You might want to practice this until you can make a fairly decent swan and then demonstrate it to students. Having demonstrated the techniques, let them experiment, either making their own swans, or making whatever they wish with the glass.

Assessing Laboratory Learning

The content objectives are best tested with written or verbal test items. Laboratory manipulative skills are best evaluated by observing individual students' work and examining materials produced (especially in the event of the extensions described above).

Primary critical thinking skills promoted by this laboratory are hypothesizing/predicting from theory and prior observations, and explaining discrepancies in results based on theory and prior observations. This is best done *via* oral questioning in pre- and post-laboratory discussion. The key criteria for evaluation include whether or not students refer to theory and prior observations to support their predictions and explanations, and the accuracy of the observations and theoretical statements used. You might want to keep a checklist to indicate a student's level of performance and to ensure that you give all students an opportunity to respond to a question either in pre-laboratory or post-laboratory discussion. If you use the responses for grading, you should realize that students who answer later questions have likely learned from their colleagues' responses and your previous probing and follow-up questions, making their educational experience quite different in both quality and quantity from those answering earlier.

DEMONSTRATIONS

Demonstration 1: Glass Bending, Blowing, and Breaking

Purpose

When setting up apparatus for various activities, it is often necessary to use glass tubing of various lengths and geometrical shapes. The following demonstration will show students how to make smooth right angle bends in glass, fire polish ends, and blow bubbles in the end of a glass tube. Also, a comparison of glass and ceramic material will be made.

Materials

Glass tubing, two pieces approximately 20 cm long
Burner
Flame spreader
Wire gauze
Ring stand

Safety

Wear protective goggles. Glass can be hot without looking hot. Use appropriate safety precautions.

Procedure

1. Cut off a piece of glass tubing 15-20 cm long by scoring the glass tube once with a triangular file. Moisten your finger with water and rub on the score. Cover with a piece of cloth and place your thumbs opposite the scratch. Apply pressure to break the glass. Fire polish by rotating the ends in a burner until the edges are rounded. Place a flame spreader on the burner and roll the tube back and forth until the glass becomes soft. Remove from the flame and hold for a few seconds. Then bend quickly into a right angle with a smooth curve. Place the glass on a wire gauze to cool. Mention that wire gauze distributes the heat. If you want your bend to be strong, cool it slowly by annealing. Glass is annealed by holding it in a "cold" yellow, smoky flame until the glass is coated with soot.
2. Obtain another piece of tubing at least 20 cm long and fire polished on the end used for blowing. Heat the unpolished end of the tube until molten and closed, remove from the flame, and blow gently into the tube, rotating the tube as you blow. This procedure may be repeated until there is a bubble that is at least twice the diameter of the tubing. Hold the tube with the bubble at the bottom until the glass hardens. Place it across a beaker to finish cooling with the bubble well away from the beaker glass.

3. Demonstrate the breakage of glass by placing a piece of hot tubing on the base of a ringstand. Remind students that this is what will happen to a hot beaker that is placed on the cool surface of a laboratory table. Discuss the fact that this broken glass can be recycled by melting and then used to make new products.
4. Examine a piece of ceramic tile that is made from clays and is strong, brittle, and heat and chemical resistant. (Examine a space shuttle tile if one is available). Demonstrate the breakage of ceramics by dropping a ceramic tile on the floor. Discuss the fact that once ceramics are broken, they may not be remelted and reformed, because ceramics are hardened by firing at high temperatures. Once hardened, they are resistant to extremely high temperatures.

Demonstration 2: Resistance through a Conductor

Purpose

In ordinary conducting materials, such as metal wire, the flowing electrons that represent current always encounter some resistance, similar to friction. The source of this resistance is the scattering of electrons from atoms that make up the conducting material. Scattering occurs if atoms are vibrating and/or if lattice defects are present. This resistance causes a loss in power between points in a circuit. Up to 20% of the total energy in an electrical circuit is wasted in transmission by resistance heating of wires. This demonstration illustrates the buildup of heat caused by resistance in an electrical circuit using an ordinary conductor.

Materials

Balloon
Battery or power supply
Nichrome wire, approximately 30 cm
Alligator clips

Safety

Use normal safety precautions when using any power source.

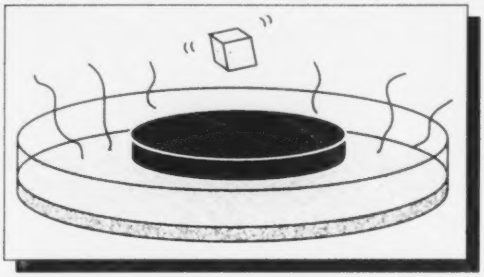
Procedure

Inflate a balloon and tape a nichrome wire or other noninsulated wire to the balloon. Attach the ends of the wire to a battery or power supply. Turn on the power source. After several minutes, the heat generated by the flow of electrons will pop the balloon.

Demonstration 3: Meissner Effect Using a Superconductor

Purpose

Moving a magnet near a superconductor induces a supercurrent (*i.e.*, a current that does not decay) within the superconductor. This supercurrent generates its own magnetic field such that the total magnetic field inside the superconductor disappears. Two opposing fields, one from the magnet and one induced by the superconductor, cause the magnet to be repelled by the superconductor, just as two like magnetic poles repel each other. If the repulsive force at the surface of the superconductor is greater than the force of gravity on the magnet, the magnet will be levitated at a distance from the superconductor. This effect can be observed when a superconductor is cooled below its critical temperature. This phenomenon was discovered by Meissner and Ochsenfeld in 1933.



In Figure 2, a magnet is levitating over a pellet of a superconducting ceramic immersed in liquid nitrogen.

Figure 2. Meissner Effect.

Materials

Kit containing superconducting ceramic pellet, magnet, and forceps.

- Kits can be obtained from science supply companies including Colorado Superconductor, P.O. Box 8223, Ft. Collins, CO 80526; Knusoft Knowledge Systems, 219 Los Cerritos Drive, Vallejo, CA 94589. Also Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706. Flinn Scientific, Inc., P.O. Box 219, 131 Flinn Street, Batavia, IL 60510; Edmund Scientific, Barrington, NJ

Liquid nitrogen (obtained from welding supply companies)
Gloves, heavy protective
Petri dish
Goggles

Safety

Liquid nitrogen is extremely cold, having a boiling point of −196 °C. Since skin contact with liquid nitrogen can result in frostbite, protective gloves that can withstand these cold temperatures must be worn. Excess liquid nitrogen should be disposed of promptly; upon standing in an open container, it can condense oxygen from the atmosphere, slowly enriching the liquid with liquid oxygen. This mixture of liquid nitrogen and liquid oxygen is a powerful oxidizer and may react violently with easily oxidized substances. The levitation activity should not be performed near flames, sparks or flammable material since powder particles from the rare-earth magnet can burn in air and create sparks. Always wear safety goggles when performing demonstrations.

Procedure

Place a pellet of the superconducting material, yttrium barium copper oxide, into a Petri dish. Using protecting gloves and goggles, pour liquid nitrogen into the Petri dish until it covers the pellet. Replenish the liquid nitrogen as it evaporates. After about a minute, the pellet should be cooled below its superconducting temperature. Pick up the magnet with plastic tweezers, and place it about 2 mm above the center of the pellet. Release the magnet and it should levitate above the pellet. Run a small piece of paper between the pellet and the magnet to demonstrate the levitation. The magnet will remain suspended until the pellet warms to above its critical temperature.

NOTE: A laboratory activity, Preparation of a Superconductor, *is presented in Extensions at the end of this module.*

Group and Discussion Activities

Key Questions

1. How can you categorize materials according to their physical properties? *[Physical properties such as boiling point, melting point, physical state, conductivity (electrical and thermal), index of refraction, ductility and brittleness are commonly used to classify materials.]*
2. What are some technological applications of ceramics and glasses? *[Ceramics and glasses have many technological applications including use in high tech rockets, space shuttle tiles, military helicopter armor, and Freon-alternative refrigerant semiconductors.]*
3. How is glass treated to make so many useful products? *[In the manufacture of glass materials (fluxes) in small amounts are added to lower the melting point of the silica and give the glass desired properties.]*

Flux Additive	***Properties***
Boron oxide	*Resistance to temperature change*
Transition metals	*Variable colors*
Potassium oxide	*Hardness suitable for grinding eyeglasses*
Lead oxide	*Crystal-like properties*
Silver chloride	*Photochromic properties for light sensitive eyeglasses*

4. What are some potential future applications for high-tech ceramic materials? *[In the future, high-tech ceramics may be used in superconducting magnets for "frictionless" trains, super high quality fiber optics for communication and information systems, and superconducting "wires" for electricity transmission.]*

Counterintuitive Examples

1. The second most abundant element in the earth's crust is silicon. Ninety-five percent of the rocks that make up the earth's crust are oxides of silicon. While silicon solar cells are useful devices for generating electricity, it takes many years of continuous electricity production for a single crystal silicon solar cell to "pay back" the energy needed to construct the device. In addition, the low level of power (voltage times current) that is generated by silicon solar cells severely restricts their applications. However, recent advances in solar cell construction have increased both their efficiency and their power rating. (Researchers are discovering how to make solar cells using polycrystalline and amorphous silicon that promise to deliver electricity at a lower cost.)
2. While ceramic material is frequently used as insulating material in the electronic industry, rare-earth composite ceramics have been discovered to be the most promising high temperature superconductors. A major problem with ceramic materials is that they are brittle and cannot be formed by machines into various shapes or drawn into wires. This is probably the biggest challenge to materials scientists who are examining ways to utilize superconducting ceramics in practical devices.

Metaphors and Analogies

Paul Grant, a scientist at the IBM Research Laboratory in Almaden, California, gives this analogy: "In a superconductor, atoms behave in such a way as to carry the electrons along with them like surfers on a wave. Because of the spin, superconductivity is really like two surfers riding on a wave, with one of them doing a head stand." The wave represents the vibration in the lattice (see *Transparency Master* in the *Appendix*).

Douglas Finnemore, a physicist at Iowa State University, compares the movement of electrons through a superconductor to a crowd moving across a football field. "If they act as individual particles, they will bump into one another and scatter. That's equivalent to electrical resistance. But suppose someone starts counting cadence, and everyone locks arms and marches in step. Then, even if a person steps into a chuckhole, he/she won't fall because the neighbors hold that person up." This is how electrons move through a superconductor.

See *Transparency Masters* in the *Appendix* for other descriptions of superconductors, conductors, and insulators. See also *Pictures in the Mind.*

Pictures in the Mind

Charge transfer by electrons is easy to understand because the moving particle itself is charged. Charge transfer by a "hole" is harder for students to visualize. To help, ask them to imagine a row of 10 chairs with 9 students sitting in the first 9 chairs. Student number 1 moves to chair number 10, leaving chair number 1 empty for student number 2. If student number 2 moves to chair number 1, that leaves chair number 2 free for student number 3, and so forth. As students move up the line, one after the other, the empty seat "moves" in the other direction. In like fashion, "holes" in the valence band move, carrying their relatively positive charge with them.

Structure of crystalline and amorphous materials. See the crystalline and amorphous structures pictured in the *Transparency Master* in the *Appendix*.

TIPS FOR THE TEACHER

Language of Chemistry

amorphous type of disordered solid lacking a crystalline structure.

annealed heated for a time just below softening temperature and then cooled.

ceramic inorganic material processed or consolidated at high temperatures. Strong bonds enable ceramics to withstand heat and chemical attack but also make them brittle.

conductor material that allows the flow of an electric current due to mobile electrons in the conduction band.

critical temperature temperature below which certain materials will conduct an electric current without resistance. This temperature is different from the critical temperature of condensed gases.

crystalline orderly arrangement assumed by a solid.

flux material that lowers the melting point of a solid.

glass amorphous homogeneous solid typically made when silica is mixed with other compounds, heated until it melts, then rapidly cooled.

insulator material in which there is no movement of electrons, due to the large gap between the valence and conduction bands.

Meissner effect ability of a superconductor to block a magnetic field and in doing so to repel any magnet that comes near it.

nonstoichiometric compound compounds that do not have a fixed ratio between the numbers of atoms in the chemical formula.

semiconductor substance that allows the flow of a slight electric current at room temperature but increases in conductivity with increasing temperature.

sintering heating at high temperatures but below the melting point to bind a powder mixture together.

superconductor material that conducts an electric current without resistance when cooled to its critical temperature.

Pattern Recognition

Silicon is a member of the carbon group and behaves somewhat like carbon. It can bind with itself to form silicon chains and oxidize to form silicon dioxide. The various silicates and aluminosilicates that make up the earth's crust contain repeating units of ionic silicon oxides. These repeating units are the building blocks for commonly found clays, sands, soils, and rocks. Construction materials such as bricks, cement, concrete, ceramics, and glasses consist largely of silicon oxides.

Repeat Unit	Si:O Ratio	Structure	Example
SiO_4^{4-}	1 : 4	Tetrahedral	Olivine
$Si_2O_7^{6-}$	1 : 3.5	Pairs of tetrahedra	Thortveitite
SiO_3^{2-}	1 : 3	Closed rings	Emerald
SiO_3^{2-}	1 : 3	Infinite single chains	Pyroxenes
$Si_4O_{11}^{6-}$	1 : 2.75	Infinite double chains	Amphiboles
$Si_2O_5^{2-}$	1 : 2.5	Infinite sheets	Talc, mica
SiO_2	1 : 2	Infinite network	Quartz, feldspars

Figure 3. Silicate structures making up the earth's crust.

Common Student Misconceptions

1. **"Glass is a crystalline solid."**

   When molten silicon dioxide (sand) is cooled, it does not crystallize. Rather it gradually becomes more and more viscous and gives rise to a stiff amorphous solid whose intermolecular interactions resemble those of a liquid. Therefore, many people prefer to describe glasses as supercooled liquids and not solids. Colored glasses can be considered metal oxide solutions in which silicon dioxide is the solvent.

2. **"Thicker bottoms on old window panes mean the glass has flowed."**

   Very old window panes are observed to be thinner at the top than at the bottom. There are two schools of thought to explain this. (1) The glass has flowed downward over the years; and (2) the glass was originally made that way. These explanations are not mutually exclusive. Students should be encouraged to research that topic. (*Sources:* Kolb and Kolb reference and Dr. William Dumbugh, Corning Glass Works, Corning, NY.)

3. **"The Law of Definite Proportions applies to all compounds."**

The Law of Definite Proportions applies to most compounds but not all. In solid state materials, the possibility exists for the formation of nonstoichiometric compounds. The copper oxide superconductor $YBa_2Cu_3O_x$, where x is approximately 7.4, is a case in point. However, nonstoichiometric compounds are never found in molecular materials.

Decision-Making

Have students analyze the benefits and costs of recycling glass. Discuss energy requirements for making and recycling glass. Compare the use of recyclable *versus* throw-away materials for various uses.

At one time, asbestos was a very common material in the construction industry. It has many desirable properties: nonflammability, flexibility, mechanical strength and inertness to chemical attack. On the other hand, airborne asbestos particles reach the lungs, do not dissolve and are not expelled. In the lungs they irritate the tissue and lead to scarring. Extensive exposure to airborne asbestos can lead to the disease *asbestosis* and to a greatly increased risk of lung cancer. Have students research the use of asbestos in the construction industry and consider the cost/benefit analysis of its use.

HISTORY: ON THE HUMAN SIDE

The oldest written records from northern Africa and the ancient Mideast all describe buildings made of bricks, which are synthetic rocks made by heating clay. The *Old Testament* of the *Bible* records that the Hebrews made bricks during the period they were held in slavery by the Egyptians. The hanging gardens of Babylon, one of the wonders of the ancient world, were built of brick. Bricks made by drying and heating in the sun were not ceramics and their lack of durability was a result. Since the technique of further heating sun-dried bricks in furnaces was known thousands of years ago, ancient fire-treating brickmakers were probably the first materials engineers.

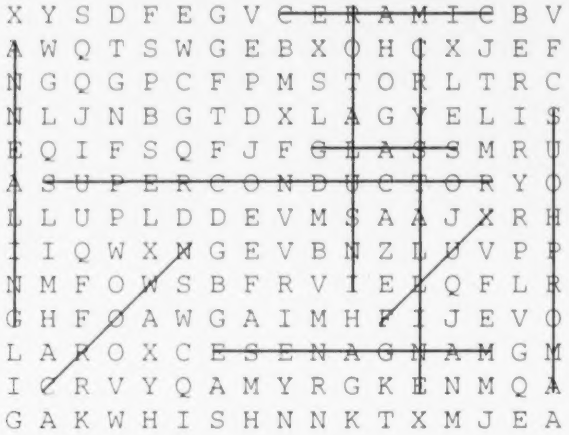
Pottery has been known for hundreds of centuries. Archaeologists use pottery shards, dish design, glazes, *etc.*, as markers for particular ancient cultures. Showing that a dig at the site of one ancient culture contains pottery from another previously identified culture is strong evidence that the two cultures traded with each other. One of the most famous forms of pottery is porcelain, manufactured by the Chinese more than a thousand years ago from a special kind of clay known as *kaolin,* named after the mountain that furnished the clay. Various Chinese emperors subsidized the porcelain industry and gave awards to potters who developed new techniques, glazes, and so forth. After Marco Polo's visits to China, Europeans began to attempt duplication of Chinese porcelain. The Germans first duplicated the Chinese process and developed a strong pottery industry based on their discoveries. The British discovered an interesting variant of the same process by adding bone ash (mostly calcium phosphate) to their pottery mix. It produced a beautiful pottery called "bone china", often called *Wedgwood China* after the original source of porcelain pottery.

Glass has also been known for many centuries, as evidenced by the glass beads found in archaeological digs. The Romans discovered glass blowing—probably around 50 B.C. In the Middle Ages, Italian and French artisans forced blown glass bubbles into various shapes and flattened them into sheets. From that discovery came a variety of bottles, jars, glasses, and stained glass windows. Experimentation with recipes and production processes also arose. Within decades of the beginning of the industrial revolution, glass products became established as economically important construction materials. Glass windows became commonplace, rather than a decoration found only in cathedrals.

Over the years, both glass (amorphous) and pottery (crystalline) ceramics were used for everything from telescope lenses to toilet bowls; the empirical knowledge on which technology depended began to accumulate. With the development of quantum theory and modern instrumentation in the twentieth century, people gradually began to understand behavior of ceramic materials. This led to both scientific and engineering revolutions in ceramic materials by the middle of the 20th century that continues to this day. Some recent products of that revolution include computer chips, optical fibers, solar cells, and high temperature superconductors. There appears to be no end to the devices that can be built of ancient clay and sand.

HUMOR: ON THE FUN SIDE

1. Message on a T-shirt: *Front*: I have no resistance.
   Back: I'm a superconductor.
2. Word Search (see *Appendix* for master copy)



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X Y S D F E G V C E R A M I C B V
A W Q T S W G E B X O H C X J E F
N G Q G P C F P M S T O R L T R C
N L J N B G T D X L A G Y E L I S
E Q I F S Q F J F G L A S S M R U
A S U P E R C O N D U C T O R Y O
L L U P L D D E V M S A A J X R H
I I Q W X N G E V B N Z L U V P P
N M F O W S B F R V I E L Q F L R
G H F O A W G A I M H F I J E V O
L A R O X C E S E N A G N A M G M
I C R V Y Q A M Y R G K E N M Q A
G A K W H I S H N N K T X M J E A
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Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Material that conducts electricity without resistance when cooled to its critical temperature.
2. Type of orderly arrangement assumed by a solid.
3. Material that lowers the melting point of a solid.
4. Material in which there is little movement of electrons.
5. Type of glass fluxed with soda ash and limestone.
6. Inorganic material with bonds strong enough to withstand heat and chemical attack.
7. Amorphous solid made from silica.
8. Compounds of this element when added to glass give it a purple color.
9. Describing a disordered solid lacking a crystalline structure.
10. Heating just below the softening temperature and then cooling.

Answers: 1. SUPERCONDUCTOR 2. CRYSTALLINE 3. FLUX 4. INSULATOR 5. CROWN 6. CERAMIC 7. GLASS 8. MANGANESE 9. AMORPHOUS 10. ANNEALING

3. Crossword Puzzle (see *Appendix*)

MEDIA

1. Nova Program on Superconductivity, 1988, 1 hr. PBS Video, 1320 Braddock Place, Alexandria, VA 22314, Telephone: 703-739-5000.
2. Superconductivity—A 10-min video produced by Wah Chang. Public Relations, Teledyne Wah Chang, 1600 Old Salem Road, Albany, OR 97321, Telephone: 503-926-4211.
3. InteractionsSeries—Wisconsin Public Television/AIT (20-min video on superconductivity). Contact: Customer Service, Agency for Instructional Technology, P.O. Box A, Bloomington, IN 47402, Telephone: 1-800-457-4509; FAX: 812-333-4278.
4. The Acme School of Stuff Series—TV Ontario—25-min programs that include segments on glass bottles (Show 6) and composite substances (Show 12). Films for the Humanities, 11 Perrine Road, Monmouth Junction, NJ 08852, Telephone: 1-800-257-5126; FAX: 609-452-1602.
5. TV Ontario has a videotape series that contains short videos that could be used in this module. Free previews are available. TV Ontario Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516.
6. The Pressware Story—A 12-min video from Corning, Inc. showing how Corelle dishes are made. Free rental from Corning, Inc., Corning, NY 14830.
7. The *World of Chemistry* (high school version) videotape "Number 18: Earth Materials." WINGS for Learning/SUNBURST, 101 Castleton Street, Pleasantville, NY 10570; (800) 321-7511; (914) 747-3310; (914) 747-4109 (FAX).
8. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
    a. *Bravais*, by Philip Pavlik. Vol. III B, No. 1, for IBM PS/2 PC-compatible computers.
    b. "Cleave," one of the programs in *Animated Demonstrations*, by Philip Pavlik. Vol. V B, No. 2, for IBM PS/2 PC-compatible computers.
    c. *Crystal Lattice*, by David Trapp. Vol. IV A, No. 1, for the Apple IIGS computer.
9. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
    a. "Liquid Nitrogen and Racquet Balls," a chapter on *The World of Chemistry: Selected Demonstrations and Animations*: Disc I (double sided, 60 min.), Special Issue 3.
    b. "Polymers," a chapter on the videodisc *Demonstrations in Organic Chemistry* (double sided, 60 min.), Special Issue 6.
10. Materials and devices available from ICE–Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-3033 (voice) or (608) 262-0381 (FAX).
    a. Memory Metal
    b. The Optical Transform Kit
    c. The Solid State Model Kit

EQUIPMENT AND INSTRUMENTATION

Furnaces, pellet-presses, crucibles (Discussion of sources of equipment used in superconductivity is included in the superconductivity laboratory activity under *Extensions and Projects*.)

Links/Connections

WITHIN CHEMISTRY

1. **Band Gap Theory and Conductors, Insulators, and Semiconductors**

Band Gap Theory explains differences in electrical conductivity among conductors, semiconductors and insulators. According to theory, atomic orbitals of atoms in a solid combine to form energy levels that extend throughout the entire solid. When many atoms interact, as in a crystal, a large number of energy levels are formed so close to each other in energy that they essentially form a continuum of levels, or **bands**, rather than the discrete quantum levels observed in atoms and simple molecules. In solids, the electrons used to hold the solid together are in the **valence band**. Electrons in energy levels that do not help hold the solid together are said to be in the **conduction band**. (The electrons not locked into bonds are free to move, and are the electrons that move when the solid conducts electricity.)

The energy distance between the valence band and the conduction band is called the band gap. Just as atoms must absorb a quantum of energy equal to the energy difference between two energy levels in order for an electron to be promoted from a lower to a higher energy level, solids must absorb a minimum quantum of energy in order to promote an electron from the highest level of the valence band to the lowest level of the conduction band. The difference between discrete molecules and solids is that, with solids, energy quanta larger than the minimum can also be absorbed. Therefore, absorption spectra of solids tend to exhibit absorption bands rather than absorption lines. In fact, this is where the name "band" originated.

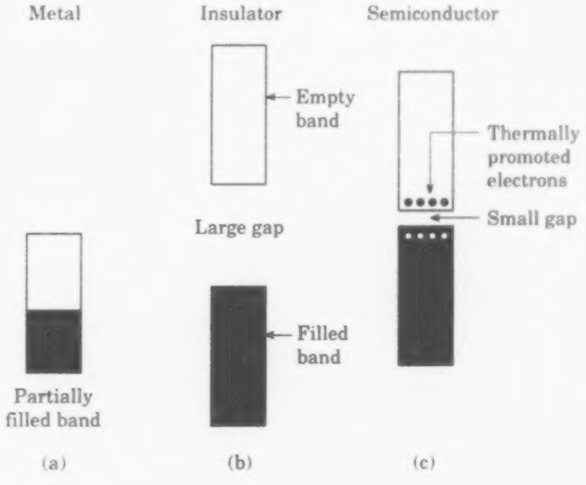

Figure 4. Band gap diagrams.

Conductivity in any solid is the result of the movement of electrons. As long as electrons are in the valence band, they are used for bonding. As soon as electrons are promoted to the conduction band, they are no longer used for bonding, and are free to move. Also, once an electron is promoted from the valence band to the conduction band, a "hole" is left in the valence band. Valence band electrons, unlike conduction band electrons, are not free to move large distances. Their movement is largely restricted to hopping over into an adjacent hole. If this movement occurs again and again, the net effect is for the hole to move (see *Pictures in the Mind*).

The magnitude of a solid's band gap determines whether the solid is a conductor, an insulator, or a semiconductor. For example, metals and certain organic polymers are characterized by having valence and conduction bands that are very close together or overlapping. Therefore, it takes very little energy to promote an electron from the valence band to the conduction band. Once in the conduction band, the electrons are no longer used for bonding and are free to move. The hole left behind in the conduction band can also move. If such a solid is exposed to an external electric field, the electrons will flow toward the positive end of the field and the holes will flow toward the negative end. Many metals have the additional advantage of having only partially filled valence bands, allowing hole migration even if electrons are not promoted to the conduction band.

In insulators, the valence and conduction bands are separated by a large energy gap. The valence band is completely filled, and no electrons reside in the conduction band. Conductivity therefore occurs only when the applied electric fields and/or absorbed energy quanta are very large. In fact, typical insulators tend to decompose when exposed to energies that are large enough to promote electrons from the valence to the conduction band. Diamond is an example of an insulator.

In semiconductors, there is a moderate difference between valence and conduction bands. Semiconduction can occur through at least three types of mechanisms. A substance that contains a completely filled valence band and a completely empty conduction band can behave as a semiconductor. This behavior is accomplished if the energy distance or band gap is small enough that electrons from the filled valence band can be promoted to energy levels in the empty conduction band by relatively small quantities of heat or light quanta. The previously empty conduction band then contains a few electrons and the previously filled valence band contains a few holes. Both electrons and holes can move under the influence of an electric field, allowing the solid to conduct electricity. Examples include silicon and other semi-metals.

When numbers of electrons are promoted to the empty conduction band as a result of absorbing light energy, electrons in the semiconductor can be made to move through a wire in an external circuit to a region where the band is empty. This mechanism is the basic principle of the silicon photocell, which is used as a source of electrical power. Some simple silicon cells can convert over 14% of the incident light to electricity. Major research efforts are currently under way to either modify silicon solar cells or to create solar cells from other kinds of semiconductors. In 1989 and 1990, composite solar cells made of two different semiconductors were reported being 25% efficient in converting incident light to electricity.

A final way to make semiconductors is by addition of impurities that either add electrons to the conduction band or holes to the valence band or both. This process is called "doping". One example of doping is the addition of arsenic to silicon to increase its conducting ability by adding electrons to the conduction band. The quantum properties of semiconductors can be finely tuned with appropriate types and concentrations of dopants. Materials scientists interested in semiconductor devices (*e.g.*, computer chips, lasers, photovoltaic cells) study the effects of dopants on semiconductor properties very carefully (see *Links and Connections, Between Chemistry and Other Disciplines* for additional discussion of semiconductors).

2. Cooper Pairs

The mechanism for low temperature superconductivity involves a notion that at first seems counterintuitive: electrons are attracted to each other to form what are called Cooper pairs. That two electrons, both negatively charged, would be attracted to each other seems to violate what is known about the law of electrostatics. The key to the attraction, though, is that a quantum property of electrons—the tendency to exist in pairs with opposite spins—is mediated by the crystal lattice of the superconductor. In a conductor like a metal, the positive ions, whose positions are fixed in the lattice, are surrounded by valence electrons of atoms that have been removed from their individual atoms and move about freely. As these electrons responsible for conductivity travel past the positive ions, the ions are drawn toward the path of the electron by electrostatic attraction.

The mechanism of conduction in a superconductor is different from that in an ordinary metal. In the superconductor, current is carried by electron pairs bound together indirectly through interaction with surrounding positive metal ions. The negative charge of an electron slightly distorts the lattice, creating a region of enhanced positive charge that attracts the second electron, accounting for the coupling of two electrons into Cooper pairs. The electrons in the pair have opposite spin moments.

At high temperatures, this coupling effect is overcome by random thermal motion of ions. However, at sufficiently low temperatures, motion of ions resulting from the passage of electrons is more important than random thermal motion. Because ions are much more massive than electrons and move more sluggishly, a "wake" of displaced positive charge is formed. At low temperatures, this wake persists long enough to attract a second electron, forming the Cooper pair. The pair is thus bound electrostatically by mutual attraction of each electron for positive ions in the lattice, and with quantum forces by having opposite spins. Because the Cooper pair is so bonded, combined momentum of the pair is not affected by its passage through the lattice.

Whereas the pair would become scattered by thermal motion of the ions at higher temperatures, it remains bound as a pair while moving at lower temperatures. Consequently, scattering does not provide energy transfer between electrons and lattice that produces resistance in a normal conductor. Nonrandom motion of electron pairs is not changed into random motion of the lattice, so energy is not "lost to heat" with the transmission of Cooper pairs of electrons. In the superconducting state, most conduction electrons are bound in Cooper pairs.

Sufficiently high temperatures and strong magnetic fields will result in fewer Cooper pairs being formed, and the superconductivity will be destroyed. Sufficiently large currents will likewise hinder the formation of Cooper pairs. Therefore, any superconductor has a characteristic critical temperature, T_c, critical field, H_c, and critical current, I_c. If any of these critical values is exceeded, superconduction will disappear.

Cooper pair formation theory is very successful in explaining and predicting properties and behavior of low temperature superconductors (mostly metals). However, the theory has been relatively unsuccessful in explaining and predicting properties and behavior of high temperature ceramic super conductors. Whether the Cooper pair theory will successfully extend to the new superconducting materials remains to be seen. It is possible that these materials work by a different mechanism entirely.

3. Nonstoichiometry of Superconducting Materials

In general, if a compound's chemical formula is checked for the valence of the elements, the algebraic sum of the total positive and negative charges is zero. In a crystalline material, each unit cell in a perfect inorganic solid contains an integral number of chemical formula units. The superconductor, $YBa_2Cu_3O_7$ is a case in point. This material superconducts at 90 K. In this case:

$$\begin{aligned} Y^{3+} &= +3 \\ 2Ba^{2+} &= +4 \\ 7\,O^{2-} &= -14 \\ 2Cu^{2+} + 1Cu^{3+} &= +7 \end{aligned}$$

For the three copper ions to have a total charge of +7, the copper ions must be present as +2 and +3 and implies one-third of the Cu is Cu^{3+} and the remainder is Cu^{2+}. Figure 5 shows an idealized structure of the superconductor, $YBa_2Cu_3O_7$.

Most new oxide superconductors are crystals with defects where there is a vacant lattice site, and oxygen deficiencies are very common. The term nonstoichiometric means there is a deviation from the ideal formula and there are vacant sites where atoms would normally be. Thus, the formula

$$La_{2-x}(BaSr)_x\,CuO_{4-y}$$

represents a nonstoichiometric formula where y is an average measure of the fraction of vacant oxygen sites in the crystal. If there is an oxygen deficiency or an oxygen excess, charge neutrality demands that the average oxidation number of one of the elements in the nonstoichiometric solid must deviate from its most common value. In the above formula, if there is an oxygen excess (or a lanthanum deficiency) the oxidation state of copper will be raised. The effect is a change in the crystal symmetry and development of a defect in the structural and chemical order of the solid. In the new high temperature superconductors, crystal defects occur on a larger scale and contribute to promoting superconducting properties.

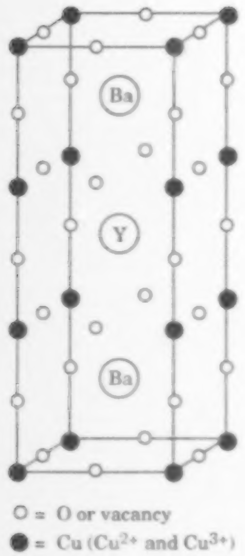

Figure 5. The unit cell structure for a perovskite superconductor made of yttrium, barium, copper, and oxygen. The formula for this material is $YBa_2Cu_3O_x$, where x is 6 or 7.

The possibility of variable oxidation states and missing oxygen or other atoms allows for the preparation of this new group of nonstoichiometric solids. Nonstoichiometric compounds do not have a fixed ratio between numbers of atoms in the chemical formula; in fact, the ratio may be continuously variable over some range. For example, iron(II) oxide has a variable composition, FeO_x with $1.05 < x < 1.13$, that does not include the stoichiometric composition $x = 1$. The possibility of forming nonstoichiometric compounds is unique to solid-state compounds and is never observed in molecular materials. It is fortunate that few nonstoichiometric compounds were known to early chemists, because ideas such as the law of definite proportions would surely not have emerged when they did, possibly delaying the progress of chemistry. Now we know that the law of definite proportions applies to most compounds, but not all; and we understand why.

4. **Network Bonding of Silicon**

See *Language of Chemistry* in *Rocks, Minerals, and Gems* module for a discussion of network bonding of silicon compounds.

5. **Intramolecular Bonding and Intermolecular Forces**

Atoms form stable units called molecules by sharing electrons. This type of sharing is called intramolecular (within the molecule) bonding. Glasses, ceramics, superconductors and semiconductors are condensed states of matter. The forces that cause the components of a substance to form liquids or solids involve covalent or ionic bonding, or may involve weaker interactions called intermolecular forces (because they occur among, rather than within, molecules). It is important to recognize when substances change from liquid to solid, the molecules remain intact. The changes in state are due to intermolecular forces rather than intramolecular forces (see *Condensed States* module).

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

1. **Electronics**

Conductivity was explained in the *Within Chemistry* section as a function of valence band and conduction band structure and band gap size. These chemical ideas can be extended to explain electronic behavior. Conductors typically decrease in conductivity as temperature increases. This behavior is explained by invoking the idea of increased random motion of ions or kernels as temperature increases. Because the band gap is small or nonexistent and numerous holes often exist in the valence band, additional thermal energy does not help conduction. Consequently, additional random motion of ions or kernels gets in the way of electrons trying to move in a nonrandom fashion.

On the other hand, the conductivity of semiconductors *increases* as the temperature increases, a behavior that is exactly opposite from the behavior of conductors and a property that is used to distinguish conductors from semiconductors. Although atoms that make up semiconductors randomly move around more as the temperature is increased, higher temperatures also provide larger energy quanta to excite electrons into the conduction band. Even though there is more blocking of current due to random atomic motion, there is much more current due to additional charge carriers. With electrons in the conduction band and holes in the valence band, the conductivity of the semiconductor increases.

The theoretical basis for doping was also explained. For example, the small conductivity of silicon can be increased at normal temperatures if the silicon crystal is *doped* with other elements. An n-type semiconductor is produced when a small fraction of silicon atoms is replaced with an element such as arsenic that has more valence electrons than silicon. Arsenic is incorporated into the silicon network *via* covalent bonds to silicon, but because silicon forms only four bonds, the extra electron on arsenic is not used for bonding. When valence and conducting bands of the As-doped silicon are formed, these extra electrons end up in the conduction band and can conduct an electric current. The term "n-doped" comes from "negative"-doping a semiconductor so that a negative charge carrier (an electron in the conduction band) is provided.

A p-type semiconductor, then, can be seen to be made by providing a positive charge carrier—a hole—in the valence band. When silicon is doped with an element that has one less valence electron than silicon, a p-type semiconductor results. Boron is an example of such a dopant because boron has only three valence electrons. An electron vacancy or hole is produced in the structure. The mechanism by which holes serve as charge carriers is explained in *Pictures in the Mind.*

The most important applications of semiconductors involve composites connecting a p-type to an n-type semiconductor to form a p-n junction. Use of p-n junctions in printed circuits has revolutionized electronics.

2. **Art and Archaeology: Stained Glass and Chemical Additives**

Stained glass windows were used as early as the 12th century to depict Christian scenes in European cathedrals. A metal or metal oxide was added to a batch of glass; this mixture was melted and then poured into molds. Colors were produced by adding d-block compounds as in the colored glass activity (see *Activity 1*). The medieval glaziers did not use pure compounds, however. Their recipes included instructions to heat substances like copper and brass until it was powdered, or to add certain kinds of powdered rocks to the glass mix.

Even the noncolored components of glass can be used to identify whether windows at one cathedral were furnished from the same source as windows at another cathedral. For example, the flux to be added to sand to lower sand's melting point nearly always included ashes of various kinds. Ashes from coastal plants are typically high in soda ash (Na_2O) whereas inland plants are typically high in potash (K_2O.) Ratios of trace elements like Pb, Zn, Mn, Fe, and others can also indicate a common or similar source for the glass.

3. **Geology: Perovskites**

Many of the new high-temperature superconductors belong to a family of ceramics called perovskites. Perovskites are ceramics (solid materials combining metallic elements with nonmetals, usually oxygen) that have a particular atomic arrangement. Perovskites are the earth's most abundant minerals and are of interest to geologists seeking clues to the planet's history. They exhibit an array of electrical properties ranging from insulators to semiconductors, superionic conductors (whole ions, rather than just electrons, flow through the crystal), metal-like conductors and now high-temperature superconductors. Some of the most interesting perovskites are rocks from volcanic magma that include latrappite, loparite and leushite, which incorporate many exotic elements in their structures, including all 14 rare-earth elements. The perovskite structure is so adaptable that these minerals act like sponges, soaking up various elements that do not fit readily into other mineral structures. Perovskites currently form the basis of a $20 billion per year electroceramics industry.

4. **Physics: Micro-Electro-Mechanical Piezoelectric Tools**

Many ceramic perovskites exhibit a property known as piezoelectricity. When an external electric field is applied to the structure, the field shifts the atoms so that the entire crystal changes shape, usually by elongation. Conversely, a mechanical deformation of some of these crystals generates an electric field. This conversion of mechanical energy into electrical energy or *vice versa* by certain perovskites can be seen in a group known collectively as PZT. For example, in the perovskite lead titanate ($PbTiO_3$) a slight compression of the crystal can result in the storage and release of a hundred volts of electrical potential. These materials are used in a wide assortment of devices including loudspeaker buzzers, electrical relays, pressure gauges, *etc.* In loudspeakers, for instance, barium titanate transducers vibrate against a membrane in response to electronic signals, generating sound waves. The most common single-crystal piezoelectric material is quartz (silicon dioxide), which is used mainly for frequency control in electrical oscillators, such as those found in watches.

5. **Geophysics and Medicine: SQUIDS**

In 1962, scientists at Cambridge University determined that a supercurrent could be induced between two superconductors separated by a thin insulating layer via a quantum-physics process called "tunneling". By directing a microwave field against the voltage, a system of measurements is created that can detect infinitesimally small magnetic fields and/or voltages. This phenomenon became the basis for an important practical application of superconductivity: superconducting quantum interference devices, or SQUIDS. These devices are used in geophysics to detect the magnetic "signatures" of minerals that indicate the presence of oil or other valuable substances underground. In brain research, SQUIDS are used to identify extremely small magnetic fields created by neurological activity.

6. **Engineering: Structural Materials**

Advanced structural ceramics are being used in a wide variety of applications ranging from scissors and tennis rackets to industrial cutting tools, engine components (engine heads, cylinders, *etc.*), heat exchangers, bearings, armored helicopters, and high-temperature rockets. They offer a combination of excellent properties including wear resistance, hardness, stiffness, and heat and corrosion resistance. They are less dense than metals and stronger at elevated temperatures. However, they also have a down side. They are brittle and sensitive to microscopic flaws like cracks, voids, and impurity inclusions. Unlike metals, they will crack and shatter under stress.

In order to remove these shortcomings, research is under way to toughen ceramics and make them more fracture-resistant. Some methods used include adding to ceramic matrices a variety of ceramic particulates, fibers, and whiskers (very strong single crystals that are at least 10 times longer than they are thick). All of these additives make the ceramic tougher by acting to deflect cracks. Whiskers and fibers can also dissipate the crack's energy through frictional forces and can actually absorb the energy of a developing crack. The addition of whiskers has yielded a composite material with five times the resistance to fracture compared to untreated ceramics.

However, progress in manufacturing ceramic parts is still plagued by inconsistent quality in the final product. Wide variations in any manufactured lot arise from the unpredictable presence of flaws in the ceramic microstructure. The flaws are due to shortcomings in the processing of ceramics and are currently an area of intense research interest.

TO THE CONTEMPORARY WORLD

Personal

Careers: Inorganic chemistry, materials science, ceramic engineering, chemical engineering, ceramics, electronics, art involving glass and pottery work, manufacturing involving ceramic and glass materials, glass conservation.

Community

1. **Field Trips**. Electronics firms, telephone laboratories (fiber optics), automobile plants, universities (computer, engineering, physics and chemistry departments), stained glass art shops, pottery shops, hospitals (MRI), ceramic tile factory, bottling company and/or beverage manufacturers.
2. **Knowledgeable Individuals**. Solid state electronics engineers (semiconductors); materials science engineers; mechanics (ceramics engineers); artisans who use stained glass, blow glass, or make pottery with enamels and glazes; NASA (spaceship tiles).

Societal (Science/Technology/Society; Current Events)

1. **Alternative to Freon**. The solid-state alternative to using Freon for refrigeration and air conditioning is present in the Peltier effect associated with particular heavily doped semiconductors. The Peltier effect is just the reverse of a thermocouple. (When a thermocouple is heated, electricity flows from the thermocouple. When electricity is forced into the thermocouple, its temperature drops.) The solid-state opportunity exists for supplementing Freon and water-based energy conversion technologies and ultimately for replacing them.
2. **Superconductors and Trains**. How soon the superconductors will go from the laboratory to the marketplace is questionable. One dream machine is a train held above a track by strong superconducting magnets. The train glides along on a cushion of air, providing a nearly frictionless ride. Maglevs are trains that operate on the principle of levitation using the old metallic superconductors and are now currently operating on an experimental basis in Europe and Japan.
3. **Ceramic Tiles and the Space Shuttle**. High-tech ceramic tiles were brought to the attention of the public in April, 1981, when a dozen of the 34,000 silica tiles on the outside of the Columbia fell off, probably during lift-off. These tiles were designed to protect the space shuttle from the 1260 °C heat of re-entry into earth's atmosphere. NASA's Ames Research Center developed a new composite consisting of 78% pure silica fibers and 22% borosilicate fibers that was less dense, more rigid, and stronger than those made solely of silica. These new tiles have been installed on the Discovery and Atlantis space shuttles.
4. **Chemical Additives in Glass Making**. When silica (empirical formula SiO_2) is heated above its melting point and cooled, glass results. The properties of glass can be varied substantially by changing the additives. For example, common glass results when Na_2CO_3 and $CaCO_3$ are added to the silica melt and then cooled. Common glass is used to make window glazing, light bulbs, drinking glasses, *etc*. The addition of B_2O_3 produces a glass called borosilicate glass that expands and contracts very little with very large temperature changes, making this glass useful for labware and cooking

utensils. Pyrex™ is an example of this type of glass. The addition of K_2O produces an especially hard glass that can be ground to the precise shapes needed for eyeglass and contact lenses. The addition of lead oxide to glass refracts (bends) light much like a gem crystal does. Even though glass is not crystalline, leaded glass can be sculpted into beautiful works of art that sparkle like crystals. Addition of silver chloride or bromide to the glass mix will produce a transparent product that darkens in bright light, producing photochromic glass for use, *e.g.*, in lenses. Titanium (II) oxide and tin(IV) oxide are added to easily melted glass to produce enamels that are used on kitchen utensils, sinks and bathtubs. Corning Glassworks alone has recorded the properties of over 250,000 glass making formulas with different additives.

5. **Glass Ceramics**. While glass is amorphous and most ceramics are crystalline, an interesting material called glass ceramics combines the features of both. The material begins as an amorphous glass; through a heat treatment process, a crystallizing agent is added, forming a polycrystalline structure. Once in this state, the glass ceramic can be machined with ordinary tools. The material can be threaded, cut into gears or similar shapes, *etc.* Space shuttle nose cones are made of glass ceramic. Pyroceram™ and Corning Ware™ are familiar brands.

6. **Emerging Technologies**
   1. ***Optical Fibers***. Currently optical fibers are silicate glasses that contain only parts per billion levels of impurities. Precise control of the refractive index is necessary to insure total internal reflection as a light beam travels down the glass fiber. These fibers are important in the communications industry as they carry thousands of simultaneous telephone messages between major switching centers. They are also used to relay signals from aircraft, to direct light to inaccessible places in medicine, and for a host of other applications. Research on longer wavelength fluoride-based glass fibers is in the very early stages and is predicted to give an order of magnitude improvement in performance of optical fibers.
   2. ***Diamond Thin Films***. Diamonds have long been characterized by their beauty, hardness and resistance to wear. But diamonds, both natural and synthetic, are often prohibitively expensive, particularly in industrial applications. Advances in materials science are now showing the way to put a coating of diamond on many other less exotic materials, thus imparting beneficial electronic and optical properties that only diamond has. This technology is based on using low pressure deposition of diamond from the vapor phase onto a supporting material. Applications of these thin films include depositing diamond films on cutting tools made of ceramics, high-quality loudspeakers made with diamond-coated tweeters, coatings for lenses, and electronics including semiconducting devices (see *Fxtensions and Projects*).

Extensions

1. **Cement and Concrete**. Cement is an aluminosilicate made by heating a powdered mixture of limestone, sand, and clay to 1500°C. The resulting solid mass is powdered and mixed with a little gypsum. When cement is mixed with water, a thick viscous material is obtained that slowly hardens as interlocking crystals of hydrated aluminosilicates are formed. Cement is usually mixed with sand, gravel, or crushed rock to give a hard, strong material known as concrete. Have students work with cement. Notice the heat given off when cement hardens. The heat is the energy released when the interlocking crystals are formed. Also notice the various properties of concrete. Measure its density.
2. **Ceramics and the History of Mankind**. Consider the societal connections to the ceramics industry. People have been making pottery since the earliest days of civilization. Students might find it interesting to examine developments in the technology of ceramics for various civilizations.
3. **Formation of Metal Silicates: A Chemical Garden**. Fill a clear jar (1-3 L) with a saturated aqueous solution of sodium silicate (water glass) and add enough salt to cover the bottom. One at a time add crystals of various transition metal salts to the solution. The metal ions react with the sodium silicate to form a thin membrane of insoluble metal silicate. Water penetrates the membrane causing it to expand and then burst. A new membrane then forms and the process repeats, causing a column of colored metal silicate to form. Different transition metal salts give rise to different colored columns.
4. **Construction of a Device to Monitor the Meissner Effect**. The following is an outline for a project in which students can closely monitor the Meissner effect, and may be a good indepth extension of the demonstration involving a floating magnet above a cooled superconductor. Materials required are an oscillator, oscilloscope, superconductor sample (with a T_c above 77 K), two small, hollow, metal coils (that can be fashioned out of wire, if necessary), styrofoam cup, and a supply of liquid nitrogen. Coils are fastened to either side of the superconductor (accomplished by several means, tape being the easiest). One of these coils is connected to the oscillator, the other to the oscilloscope, effectively linking the oscillator to the oscilloscope, *via* the alternating magnetic field between the coils. A visual representation of the oscillator's signal will be evident on the oscilloscope's screen. At this point, liquid nitrogen can be poured onto the coil-superconductor assembly in the cup. When the superconductor cools to its critical temperature, it will block out the magnetic field linking the coils, in accordance with the Meissner effect, and the signal represented on the oscilloscope will simultaneously plummet.

   Devices based on this concept can be tied into a cryostatic system, which can then measure a superconductor's T_c without having to make any electrical connections to it (a sometimes tedious process when performed on ceramics).

   Further information on this project can be obtained from:
   Robert Bristol, 1198 Marigold N.E., Keizer, OR 97303

LABORATORY ACTIVITY: STUDENT VERSION

Extension Activity: Preparation of a Superconductor

Purpose

To prepare Yttrium 1-2-3 superconductor that has the formula $YBa_2Cu_3O_8$ and test for superconductivity using a small magnet.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Many of the materials used for preparing superconductors are toxic. You should wear rubber or plastic gloves, work in the fume hood and wear a dust mask in addition to wearing safety goggles. Any leftover materials should be disposed of as your teacher directs.
3. Because you will be heating samples to very high temperatures (900-1000 °C), you should be very careful with potentially hot materials.
4. Liquid nitrogen is also quite dangerous. If you spill liquid nitrogen on you, the part of the body that comes into contact with liquid nitrogen will become frostbitten. Don't play with liquid nitrogen. The most immediate danger from carelessness (as opposed to horseplay) is from having your feet under the table on which you are working. Liquid nitrogen flows very rapidly when spilled and will often roll off the table. Adopt a stance such that any liquid nitrogen flowing off the table will land on the floor, not on your shoes.
5. In addition, you will attempt to levitate small rare-earth magnets with your superconducting pellet. The levitation activity should not be performed near flames, sparks or flammable materials, since powder particles from the rare-earth magnet can burn in the air and create sparks.

Procedure

1. Calculate the correct masses of yttrium oxide, Y_2O_3, barium oxide, BaO, and copper oxide, CuO, such that you get a mole ratio of 1 Y to 2 Ba to 3 Cu. Remember that one mole of yttrium oxide contains two moles of yttrium ions. Your teacher will inform you what the total mass of the mixture should be.
2. Measure the previously calculated masses on a balance that is precise to at least 0.01 g and mix the measured powders in a mortar.
3. Grind the powders together with a pestle. The better you do this job, the more likely your final pellet will be a superconductor. A key to this step is to grind until you are too tired to grind any more, and then have your laboratory partner do the same.
4. Following the directions of your teacher for the pellet press you are to use, press the powder you have just ground into a pellet. Again, the firmer the pellet, the more likely the final product will be a superconductor.
5. Place your pellet in a crucible. The crucible should either be uniquely marked, or you should put it in a location in the oven that will allow you to identify it as yours when you take it out of the oven. Put the crucible in the oven.
6. When all classmates have prepared their pellets and put them in the oven, set the oven to a maximum temperature of 950 °C, turn the oven on, and let the pellets cook overnight. If your school has only one oven, your teacher may choose to have everyone put their pellets in and turn the oven on after the last class. The pellets should "cook" for at least 12 hr. If the oven you are using has an especially air-tight door (many pottery ovens in art shops can be made

air tight so that glazes are fired in a reducing atmosphere), you or your teacher may want to crack the door occasionally to admit more oxygen as the pellets are heating. (Many scientists who prepare superconductors go to the extra trouble of having oxygen flowing into the oven during pellet heating.)

7. After the pellets have heated overnight at 950 °C, set the oven to 400 °C, and "cook" at this lower temperature overnight.
8. After the pellets have heated overnight at 400 °C, turn the oven off and let the oven cool overnight without opening the door.
9. To test your pellet for superconductivity, proceed as follows (see Figure A).

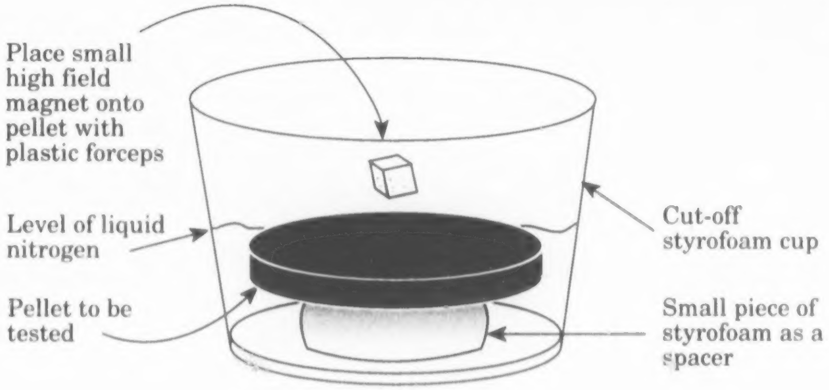
Place small high field magnet onto pellet with plastic forceps
Level of liquid nitrogen
Pellet to be tested
Cut-off styrofoam cup
Small piece of styrofoam as a spacer

Figure A. Testing for superconductivity.

   a. Place the pellet in a cut-off styrofoam cup, preferably on a styrofoam spacer.
   b. Pour liquid nitrogen into the cup until it just covers the pellet to be tested. (The liquid nitrogen will bubble and vaporize until the pellet and the inside of the cup are at liquid nitrogen temperature.) Add more liquid nitrogen before the pellet cools to liquid nitrogen temperature while it is still partially immersed, as indicated in the figure.
   c. Slowly and carefully lower a small powerful magnet above the pellet. (The samarium cobalt magnets found in old "Walkman" earphones work well.) It is better to use plastic forceps to place the magnet, but you can also place it by tying a light thread to it and lowering it to the surface of the pellet. To avoid frostbite ***do not*** use your fingers!
   d. If the magnet floats above the pellet, the pellet is a superconductor.

10. If time permits, use styrofoam balls of different sizes to build a model of the Yttrium 1-2-3 unit cell. Your teacher may choose to have you do this step during some of the cooling time.
11. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

Observe the magnet floating above your superconductor. Imagine the magnetic lines of force you would observe if you sprinkled iron filings around that magnet in three dimensions. Now imagine that the pellet is refusing to allow those lines of force to enter its surface. The magnetic lines of force, and the magnet, are being pushed away—repelled.

Look at the model you have built or a picture of a perovskite superconductor made of yttrium, barium, copper, and oxygen. Imagine the electrons moving along the plane containing Cu and O atoms such that even electrons very far from each other are spin-paired. They are dance partners—when one moves, the other makes a mirror image move.

Implications and Applications

1. Magnetically levitated trains and subways are one way of using the Meissner effect industrially to minimize friction and maximize fuel efficiency. What are some other ways the Meissner effect might be used?
2. Look at the Periodic Table. What metal oxides might be used in place of yttrium oxide, Y_2O_3, barium oxide, BaO, and copper oxide, CuO, in making a 1-2-3 superconductor? *(HINT: Both the charge and the size of the metal ion are important. The Cu-O sheets in the unit cell structure seem to be necessary for superconductivity to occur in these compounds.)*
3. Most high T_c ceramic superconductors need to be protected from the air because they react with water vapor and carbon dioxide. Use the Periodic Table to explain why this might be true.
4. Many applications of superconductors require that they be in coils of wire. With the high T_c compounds, why might that be a problem?

LABORATORY ACTIVITY: TEACHER NOTES

Extension Activity: Preparation of a Superconductor

Introduction

The purpose of this activity is to prepare high temperature superconductors, a very exciting class of materials first discovered in the mid-1980s. Superconductors are already used in scientific instruments such as magnetic resonance imaging (MRI) and are potentially useful in areas like energy storage and magnetic levitation. Superconductivity is a special property of some materials such that below a given temperature called the *critical temperature* or T_c, the material conducts electric current without resistance.

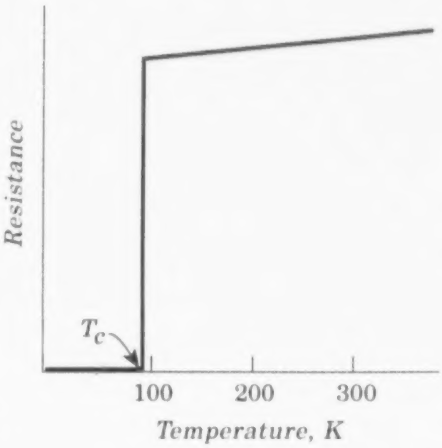

Figure B. This graph shows the resistance versus temperature of the superconductor $YBa_2Cu_3O_{6.5}$, which super-conducts below 92 K. The resistance falls to zero at the T_c.

The first group of superconductors, discovered in 1918, were metals that lost all resistance when cooled to a temperature near zero Kelvin. For years, these were the only superconductors known, and had to be studied at the temperature of liquid helium. The explanation for this property was that it arose from long distance spin pairing of electrons within solids. The movement of electrons within a superconducting solid could then be compared to the movement of a crowd of people who have decided to move to a counted cadence. If everyone in a crowd leaving a ballgame decided to get through the only gate on their own, there would be a lot of random milling around, bumping into each other, and scattering. This disorganized process would resemble regular electric current with lots of resistance. If the crowd were lined up in ranks just wide enough to get through the gate and then marched out the gate to the same cadence, they'd get out much more quickly with little or no jostling, bumping and random movement. This latter arrangement resembles low temperature superconductors.

In the mid-1980s, some ceramic oxide materials were discovered to be superconducting. Not only that, they were superconducting at temperatures that were much higher than the previously known superconductors. In fact, many became superconducting at temperatures higher than the temperature of liquid nitrogen—a very cold liquid (77 K) compared with room temperature, but very hot compared with the temperature of liquid helium (4 K). The old theory of long range spin pairing of electrons was not adequate for explaining all of the behaviors of these new materials, and no completely successful theory has been developed to explain and predict the behavior of high T_c ceramic superconductors.

One of the interesting properties of superconductors is that they block magnetic fields. Because of this blocking effect, they serve as a sort of anti-magnetic mirror, reflecting any magnet that comes near them. This behavior leads to something called the **Meissner Effect**—the ability of a superconductor to make a magnet float above it, no matter what the orientation of the magnet or the superconductor.

Major Chemical Concept

The major chemical concept depends on what you wish to do with this activity. Periodic properties and a comparison of metallic, reaction stoichiometry, ionic, and covalent network bonding in solids, the possibility for solids reacting with each other, and colligative properties (melting point lowering at the grain boundaries) are a few of the chemical concepts related to this laboratory.

Level

General and honor students.

Expected Student Background

The expected student background depends on what concepts are treated. A knowledge of stoichiometry and periodic properties appear to be the minimum if students are to develop an understanding at deeper than the cookbook level. However, preparing real superconductors is fun, even if it is done as a cookbook exercise.

Time

Calculating stoichiometric masses of ingredients and preparing pellets will take a full 40-45 min period. Conducting a Meissner Effect test requires only a few minutes. (Note that two overnight heatings and one overnight cooling of the pellets is required before students can conduct the Meissner test.)

Safety

Read the *Safety Considerations* in the *Student Version*. It is quite important that students wear dust masks and wash their hands thoroughly after preparing their pellets. Liquid nitrogen safety should be rigorously enforced so make sure students follow safety procedures outlined in the *Student Version*.

Materials (For 24 students working in pairs)

Nonconsumables

12-24 Ceramic crucibles
12 Mortars and pestles
Balance (0.01 or 0.001 g precision)
12 Spatulas
Pellet press
12 Crucible tongs
Furnace
Thread or plastic forceps
12 Styrofoam cups
Scissors (to cut the styrofoam)
Small lightweight powerful magnet (like the Samarium-Cobalt magnets sold by science supply houses or found in cheap "Walkman" headphones)
Transparency master of Yttrium 1-2-3 unit cell

Consumables (see *Advance Preparation* for further information)

Yttrium oxide, Y_2O_3
Barium oxide, BaO
Copper oxide, CuO
Other oxides *(optional)*
Styrofoam balls
Stiff wire, long pipe cleaners or toothpicks

Advance Preparation

Materials must be ordered and arranged in advance. Most high schools cannot support this activity with supplies available in the storeroom.

Needed consumables depend on the laboratory. If students are to conduct this laboratory as described with no additional metal oxides tested, they need a source of yttrium oxide (Y_2O_3), barium oxide (BaO), and copper oxide (CuO). The amount of oxides needed depends on the size of pellets to be made and the number of student groups. If other oxides are to be used, students need those as well. If students are to build models of 1-2-3 compounds, they should also have styrofoam balls, stiff wire or long pipe cleaners, toothpicks, *etc.* The transparency master showing the structure of the Yttrium 1-2-3 unit cell will be needed for discussion as well as for reference during model building.

Kits

Arbor Scientific, P.O. Box 2750, Ann Arbor, MI 48106-2750 sells a kit (1990 price: $275) for conducting this laboratory that includes everything except the balance and the furnace. The oxides sell for $100. Even if you don't purchase the kit, you may want to get their catalog so you can show your school's industrial arts teacher a picture of their pellet press so one can be made at school. Many science education supply companies carry kits produced by Colorado Superconductor, P.O. Box 8223, Fort Collins, CO 80526. Knusoft Knowledge Systems, 219 Los Cerritos Drive, Vallejo, CA 94589, and I.C.E., Project 1-2-3, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706 also supply kits.

Metal Oxide Powders

Sources of metal oxide powders, including unusual ones like gadolinium oxide, Gd_2O_3, include: Alfa Products, Division of Morton Thiokol, 152 Andover Street, Danvers, MA 01923; Fluka Chemical Corp., 980 South 2nd Street, Ronkonkoma, NY 11779; and Cera/Pure Division, Box 1178, Milwaukee, WI 53201. (Alfa generally, but not always, has the best prices.)

Furnace

Any furnace that will serve to fire crucibles for gravimetric analysis will probably work fine. Numerous science suppliers carry small furnaces. Small Thermolyne furnaces are relatively inexpensive, easy for a nonmechanic to trouble-shoot and repair using the furnished manual, and useful for activities other than superconductor preparation (*e.g.*, the glass laboratory activity). Many science teachers have reported successfully preparing superconducting pellets in furnaces used for firing pottery. (See your art teacher about using the pottery kiln.)

Pellet Press

Pellet presses are easily made in a machine shop. The Arbor Scientific pellet press is a good model for such homemade presses. If you wish to purchase a small hand-operated press, write the Parr Instrument Company, 211 Fifty-Third Street, Moline, IL 61625.

Liquid Nitrogen

There should be numerous sources of liquid nitrogen in any fair-sized city. Liquid nitrogen is used by factories, foundries, universities and colleges, hospitals, doctors' offices, welding shops, plumbers' supply stores, *etc.* Ask around. The places that sell liquid nitrogen will also rent Dewar flasks (laboratory thermos jugs). If you do this activity a lot and want to purchase a Dewar flask, one source is Pope Scientific, P.O. Box 495, Menomonee Falls, WI 53051.

Magnets

Suitable magnets can be found by dissecting dead headphones from "Walkman" type recorders and radios. Samarium-cobalt magnets can also be ordered from Edmund Scientific, 101 E. Gloucester Pike, Barrington, NJ 08007; (609) 573-6250; (609) 573-6295 (FAX).

Since the *Introduction* mentions that superconductors find application in magnetic resonance imaging (MRI), you may wish to refer to the information about MRI presented in *Pictures in the Mind* in the *Instrumentation* module.

Pre-Laboratory Discussion

The pre-laboratory you use depends on the goals you wish to promote. This laboratory can be treated as an attempt to synthesize a compound that has some interesting and potentially useful properties, an activity many professional chemists engage in. One approach might be to use the second *Implications and Applications* question to structure the pre-laboratory discussion. After students predicted which metal oxides might be substituted for Y_2O_3, BaO, and CuO, they would prepare regular Yttrium 1-2-3 and the substituted compound.

If you wish to lecture on the nature of high Tc superconductors, you should read some of the articles written for general readers and teachers (see the first five references under *References* at the end of this module).

If you plan to have students build models of the Yttrium 1-2-3 unit cell, discuss the transparency master and discuss model building.

Teacher-Student Interaction

Because this is a cookbook type laboratory, your role should mostly be enforcing safety standards. Once students begin to test their pellets for superconductivity, you should ask them to explain the test, to tell other students how they made their pellet if more than one recipe is used, and so forth.

Anticipated Student Results

Many students have successfully prepared superconducting pellets using the recipes and directions given here. However, many have failed for reasons that are not well understood. There is apparently some luck involved in getting the right amount of oxygen into a furnace that does not have a continuous oxygen supply. Sometimes two different pellets pressed from the same mixture and cooked side by side in the same furnace give different results, one providing a positive Meissner test and the other testing negative.

Answers to Implications and Applications

1. Many responses are possible to this open-ended question.
2. Any 3+ ion with almost the same ionic radius as Y is acceptable as a Y substitute. Both lanthanides and *p*-block scandium group and vanadium group metals are potential substitutes for Y and many researchers have tried them. Students will typically propose Ni(II) and Zn(II) as substitutes for Cu(II). Some students may also propose substituting Ag, Au, and Hg for Cu. Ca and Sr are typically proposed as substitutes for Ba.

3. The high T_c ceramics are metal oxides, that are typically basic. Carbon dioxide is an acid and reacts with the basic oxides to make carbonates. Water also acts as an acid, reacting with the metal oxides to produce hydroxides. Both carbonate and hydroxide deform the crystal structure as well as changing the chemical nature of the oxygen atoms in the ceramic compound. This question provides a good opportunity to review previously studied reactions.
4. Making materials into wires requires that they be malleable and ductile. Ceramics are brittle and will break if drawn or bent. There have been numerous attempts to overcome this problem. Ask students for suggestions—*e.g.*, cast the ceramic in the shape required, mix the ceramic with metal so that the wire is malleable and ductile and parts of it are still superconducting, *etc*. The brittleness of the high T_c superconductors shows quite clearly why industrially useful materials must have several useful properties, not just one.

Post-Laboratory Discussion

See *Teacher-Student Interaction*. Your post-laboratory discussion will be guided by the specific content objectives you have chosen to emphasize. If you have conducted this laboratory as an activity to determine what might be substituted for Y, Ba, and Cu, you should have students compare results with predictions. Slight changes in geometry or electron structure might cause large changes in superconductivity behavior.

Extensions

There are numerous extensions. In addition to trying substitute metal oxides in preparing 1-2-3 compounds, students can attempt to synthesize other combinations. High school students have successfully prepared $M_2M'_2M''_1Cu_2O_x$ and $M_2M'_2M''_2Cu_3O_x$ where M = aluminum or nitrogen group (*p*-block) metal such as Tl or Bi, M' and M" = alkaline earth metal such as Ca, Ba, or Sr. (*Check the toxicity of these compounds before proceeding.*) Thallium compounds are especially toxic. Stoichiometric quantities of oxides or carbonates are typically ground together repeatedly, pressed into pellets, and heated at 900 °C for 5-10 min. Superconductivity is apparently destroyed if they get hot enough to melt at the grain boundaries between the powder grains. Safety precautions must be observed.

Students may wish to actually measure the T_c of a superconducting pellet. The kits cited above are best for that exercise, but students can do it without a kit if they are careful. Students should prepare a thermocouple from thermocouple wire as thin as they can get. (Omega Engineering, Box 407, Stamford, CT 06907 is the absolute best source of thermocouple materials and their catalogs contain lots of instructional materials as well, including how to use thermocouples.) Students can insert the thermocouple into a pellet either by using a tiny drill to drill a hole in the side of the pellet for thermocouple insertion, or by placing the thermocouple between two identical pellets that are then glued together with silicon sealer. (This is the technique used for some kits.) The thermocouple is connected to an appropriate millivolt meter and the thermocoupled pellet is cooled until it exhibits the Meissner effect. Students should then let the pellet gradually warm until the magnet is observed to sink down onto the pellet. The temperature at that point is approximately the critical temperature.

If your school has the appropriate apparatus, you may also measure the critical current, I_c (the maximum current a superconductor can carry without losing its superconductivity), and the critical field, H_c (the maximum magnetic field a superconductor can withstand without losing its superconductivity).

Assessing Laboratory Learning

1. Evaluate the stoichiometry calculations produced by students in order to arrive at the correct mass of each reactant.
2. The approach to producing the superconducting ceramic pellet is straightforward and "cookbook" in nature. However, there are many new laboratory experiences involving pellet presses, high-temperature ovens, *etc.* These procedures can be evaluated by observing the student's adherence to the instructions.
3. The activity objective is to produce a superconducting ceramic pellet. Evaluate each student-made pellet by placing it in liquid nitrogen and testing it with a magnet. Does the magnet levitate, illustrating the Meissner Effect?
4. Have students describe the Meissner Effect.
5. Ask students to list problems in producing a ceramic pellet that superconducts.
6. If students have built a model of a Yttrium 1-2-3 superconductor, compare the model with the structure of the perovskite superconductor found in *Links and Connections*.

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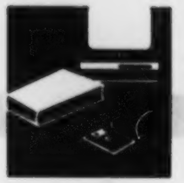

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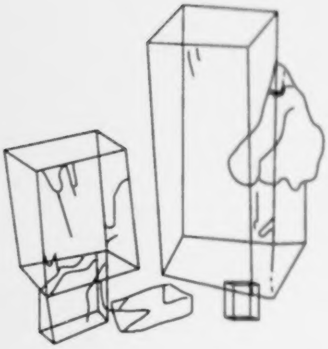
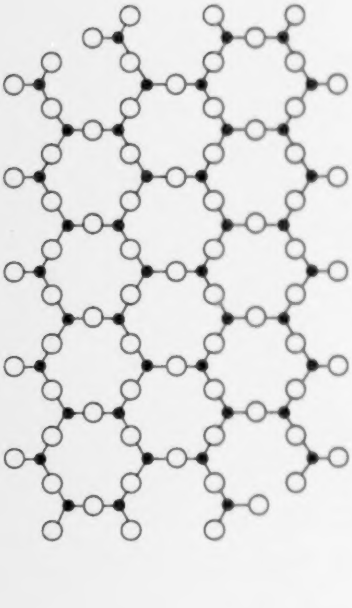
Appendix

- **Transparency Masters**
  1. Structure of Crystalline and Amorphous Solids
  2. Current Flow and Resistance in Insulators, Conductors, and Superconductors
  3. Superconductivity Analogy
  4. Yttrium 1-2-3 Unit Cell
  5. Word Search
  6. Materials Science Crossword Puzzle

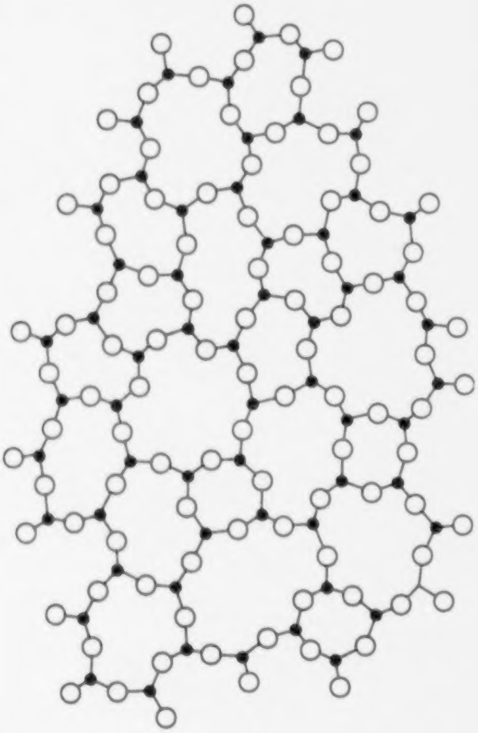
Structure of Crystalline and Amorphous Solids



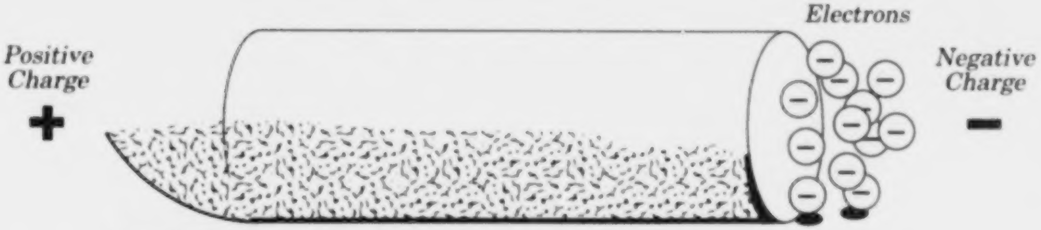
Crystalline



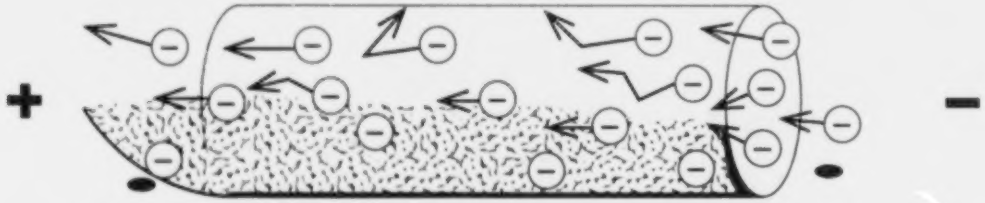
Amorphous
(Glass)



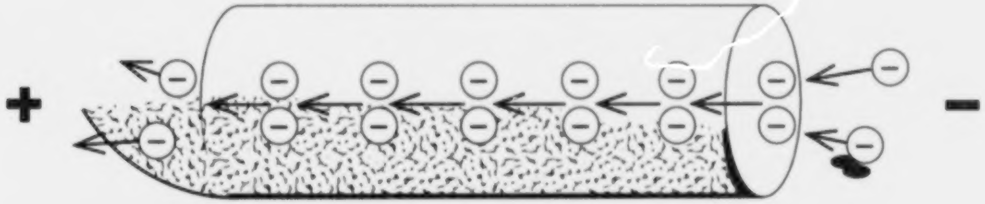
Current Flow and Resistance in Insulators, Conductors, and Superconductors



INSULATOR In materials with extremely high resistance, such as rubber or glass, electrons are tightly bound to atoms and cannot be jostled loose to sustain a flow of current.



CONDUCTOR In materials with lower resistance, some electrons are loosely bound and form a current when voltage is applied. Resistance is a measure of the energy lost in the form of heat from electron collisions.



SUPERCONDUCTOR When materials become superconductive, all resistance disappears because electrons are bound into pairs, which move in step with each other, avoiding collisions. Current flows with no energy loss.

Superconductivity Analogy

Conductivity

- Electricity is motion of electrons
- Electrons hit atoms = resistance

FREE ELECTRONS

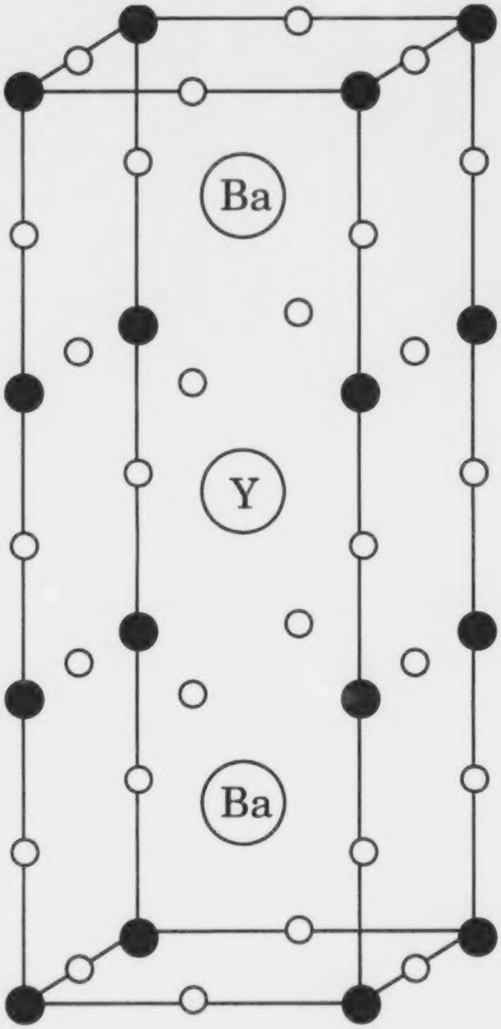
Superconductivity

- No resistance
- Electrons c-c-c-catch the *wave!!* but—only when they are cold

SUPERCONDUCTING PAIRS

Courtesy of Dr. A. M. Stacy, University of California Berkeley

Yttrium 1-2-3 Unit Cell



○ = O or vacancy

● = Cu (Cu^{2+} and Cu^{3+})

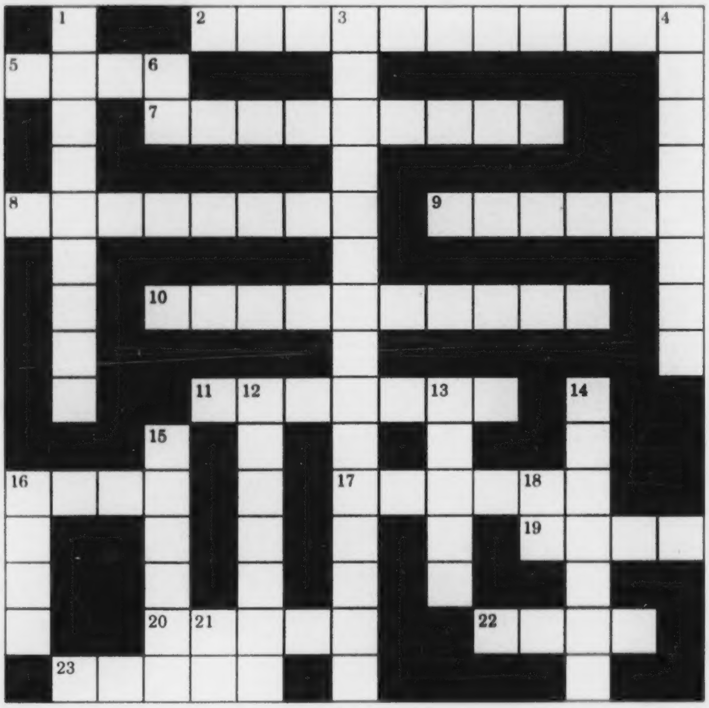
Word Search

X Y S D F E G V C E R A M I C B V
A W Q T S W G E B X O H C X J E F
N G Q G P C F P M S T O R L T R C
N L J N B G T D X L A G Y E L I S
E Q I F S Q F J F G L A S S M R U
A S U P E R C O N D U C T O R Y O
L L U P L D D E V M S A A J X R H
I I Q W X N G E V B N Z L U V P P
N M F O W S B F R V I E L Q F L R
G H F O A W G A I M H F I J E V O
L A R O X C E S E N A G N A M G M
I C R V Y Q A M Y R G K E N M Q A
G A K W H I S H N N K T X M J E A

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Material that conducts electricity without resistance when cooled to its critical temperature.
2. Type of orderly arrangement assumed by a solid.
3. Material that lowers the melting point of a solid.
4. Material in which there is little movement of electrons.
5. Type of glass fluxed with soda ash and limestone.
6. Inorganic material with bonds strong enough to withstand heat and chemical attack.
7. Amorphous solid made from silica.
8. Compounds of this element when added to glass give it a purple color.
9. Describing a disordered solid lacking a crystalline structure.
10. Heating just below the softening temperature and then cooling.

Materials Science Crossword Puzzle



Across

2. Adjective describing a solid with a regular arrangement of its components.
5. Adjective describing the melting points of ceramic materials.
7. Type of solid with considerable disorder in its structure.
8. With 9-Across, ability of a superconductor to block a magnetic field.
9. See 8-Across.
10. Adjective describing the structure of certain substances like glass that allows it to transmit light equally in all directions.
11. Theory that accounts for the differences in electrical conductivity of substances due to the size of a gap in the energy levels of atomic arrays (2 words).
16. Prefix meaning "half," and used with the word conductor to denote substances whose electrical conductivity increases appreciably as the temperature increases.
17. With 22-Across, electrons with opposite spin which are responsible for most of the conducting electrons in a superconductor.
19. Word with earth or gas.
20. Physical property of many glasses and ceramic materials.
22. See 17-Across.
23. Amorphous solid obtained by fluxing silica and cooling rapidly.

Down

1. Process of heating at high temperature, but below the melting point of the various components.
3. Materials that conduct electricity without resistance when cooled to their critical temperatures.
4. Particle whose movement is facilitated when an impurity is added to a semi-conductor.
6. Symbol for element No. 105 as suggested by its discoverer, Ghiorso, but not adopted by the International Union of Pure and Applied Chemistry.
12. Heats a substance for a time just below its softening temperature and then cools it.
13. Fundamental particles that make up all materials.
14. Inorganic, nonmetallic material processed and hardened by firing at high temperatures.
15. Component of glass.
16. Property of 4-Down.
18. Element No. 68 (Symbol).
21. Element No. 76 (Symbol).

Across

2. CRYSTALLINE
5. HIGH
7. AMORPHOUS
8. MEISSNER
9. EFFECT
10. ISOMORPHIC
11. BAND GAP
16. SEMI
17. COOPER
19. RARE
20. COLOR
22. PAIR
23. GLASS

Down

1. SINTERING
3. SUPERCONDUCTORS
4. ELECTRON
6. Ha
12. ANNEALS
13. ATOMS
14. CERAMIC
15. SILICA
16. SPIN
18. Er
21. Os

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CHEMISTRY IN MEDICINE

ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

The average life expectancy of U.S. citizens in 1990 was about 75 years, quite a contrast to a life expectancy of 68 in 1950 and of 60 in 1930. Chemistry and technology have played important roles in increasing the life expectancy and in improving the quality of life. Our increasing knowledge and understanding of the chemistry of biological processes and the discovery of therapeutic medical compounds (drugs) have contributed to the improvement of both mental and physical health and the quality and length of life.

A drug is a substance that can change a physical or psychological function in the body. Drugs may have both desirable therapeutic properties and undesirable side effects. Familiar substances like aspirin, antibiotics, alcohol, nicotine, *etc.*, are drugs. When should a specific drug be used? The media often try to help make that decision through advertising. Teenagers are highly susceptible to the advertised message, and sometimes the message is correct. You can get rid of a headache with aspirin ("I have occasional aches and pains, and, when I do, my friend Bufferin is there to help me."), you can relieve an upset stomach with an antacid tablet ("Plop, plop! Fizz, fizz!"), and some first-aid ointments can help prevent infection and relieve pain ("Exclusive Formula! The three antibiotic ingredients widely recommended and used...plus an extra ingredient to relieve pain fast!"). Yet sometimes the properties of these substances may be independent of advertised claims.

On the other hand, the media message is often misleading. Some beer commercials, for example, try to lead people to believe that copious beer drinking can make one the life of the party and part of the in-crowd. This treatment of alcohol use is misleading and dishonest. Studies have shown that alcohol impairment does not make a person more gregarious and fun-loving, but rather leads to central nervous system depression and introversion. Indeed, government regulations now require truth in labeling, as the following typical warning on a whiskey label states: "...According to the Surgeon General, women should not drink alcoholic beverages during pregnancy because of the risk of birth defects; consumption of alcoholic beverages impairs your ability to drive a car or operate machinery, and may cause health problems..."

The purpose of this module is to inform students about the many positive uses of compounds used in medicine. These therapeutic drugs, some of which can be obtained over the counter, represent a variety of substances that help us cope with daily stress or disease. Yet, some of these substances (alcohol, tobacco, anabolic steroids) can be used illegally and abused. It is important that high school students understand the chemistry of drugs.

PLACE IN THE CURRICULUM

This module can be used as a supplement to an introductory organic chemistry module, or as the basis for enrichment through special projects and/or independent study.

CENTRAL CONCEPTS

1. The application of the principles of chemistry (and biology) to the introduction of new therapeutic agents is called medicinal chemistry. The medicinal chemist must have a knowledge of general and organic chemistry and biological sciences.

2. A therapeutic agent is often called a drug. A drug is any absorbed substance that changes any physical or psychological function in the body.
3. Physicians prescribe drugs to fight infection (antibiotics), reverse a disease process (heart stimulants), restore normal function (insulin), aid in diagnosis (radiopharmaceuticals), inhibit normal body processes (birth control pills), and maintain health (vitamins and vaccines).
4. Consumers use drugs to relieve common symptoms of discomfort (aspirin, cold remedies, antihistamines, antibiotics), to supplement the diet (vitamins), to enhance or inhibit normal body functions (sleeping pills, birth control pills, stimulants), *etc.*
5. Some people abuse drugs. Any drug can be abused, but the commonly abused drugs are alcohol, stimulants, depressants, opiates, tetrahydrocannabinol, nicotine, and anabolic steroids.
6. Drugs affect the living system, perform their action, and are eliminated from the body. Addiction, withdrawal, and tolerance are possible.
7. Drugs are known by brand names, generic names, and street names.
8. Drug sources are plants, animals, microorganisms, and laboratory synthesis.
9. Information about drugs can be obtained from the *Physician's Desk Reference* (PDR), *PDR for Nonprescription Drugs*, *The Merck Index*, and package label inserts.

RELATED CONCEPTS

1. Elementary biology
2. Brief introduction to organic chemistry (*e.g.*, nomenclature, identification of functional groups)

RELATED SKILLS

1. Manipulative laboratory skills involving the use of common glassware and hardware are needed to perform the activities in this module.

PERFORMANCE OBJECTIVES

After completing their study of chemistry in medicine, students should be able to:

1. discuss a drug as any substance that will produce a change in the physical or psychological function of the body.
2. recognize medicinal chemistry as a link between chemistry and human biology.
3. differentiate between common drug terminology and scientific nomenclature.
4. state where to find information about drugs.
5. recognize that all drugs have positive and negative effects.
6. discuss the medicinal reasons and social reasons for drug usage.

Concept/Skills Development

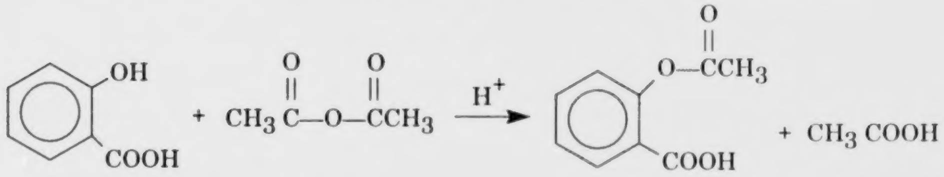
Laboratory Activity: Student Version

Activity 1: Synthesis of Aspirin

Introduction

In this laboratory activity you will synthesize aspirin, a derivative of salicylic acid. Salicylic acid and its derivatives are antipyretics. Such compounds lower the body temperature of a person with a fever. They have little effect if the body temperature is normal. Salicylates are also mild analgesics that relieve pain associated with headache, neuralgia, and rheumatism. Salicylic acid itself is not used for these purposes because it has an irritating effect on the stomach.

The most common salicylate used in medicine today is aspirin. In this activity, aspirin is prepared from salicylic acid and acetic anhydride.



When ingested, aspirin (acetylsalicylic acid) passes through the stomach largely unchanged. It is hydrolyzed in the intestinal tract liberating the active ingredient, salicylic acid.

In this laboratory synthesis, you will heat a mixture of salicylic acid and acetic anhydride with a trace of sulfuric acid as catalyst. Because aspirin is not very soluble in water, it can be isolated by addition of cold water to the reaction mixture followed by a gravity filtration.

Purpose

To synthesize aspirin from salicylic acid, test for the purity of the product obtained, and determine the number of aspirin tablets that can be obtained from your preparation.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Acetic anhydride is irritating in the liquid and vapor state. Avoid contact with skin and eyes. Rinse with water any body area that comes in contact with acetic anhydride.
3. Concentrated sulfuric acid is a powerful dehydrating agent; handle it carefully to avoid contact with skin and clothing.
4. Methanol is toxic; breathing its vapors and skin contact with methanol should be avoided.

Procedure

1. Set up a ring stand with a ring, wire gauze, and burner. The top of the burner should be about 12 cm below the ring and wire gauze. Place on the wire gauze a 400-mL beaker half-filled with water. Heat the water to boiling. This is your water bath. As you wait for the water to boil, go to the next step.

2. Weigh 2.0 g salicylic acid on weighing paper, and transfer the solid to a 125-mL Erlenmeyer flask.
3. Add 5 mL acetic anhydride from a 50-mL buret.
4. Add 5 drops concentrated sulfuric acid. (*CAUTION: Sulfuric acid is corrosive.*) Stir the mixture.
5. Heat the flask in the boiling water bath for 10 min.
6. Remove the flask from the water bath, and carefully add 2 mL water from a 10-mL graduated cylinder. Swirl to mix the contents. Allow the flask to stand for 5 min.
7. Add 40 mL water from a graduated cylinder, and stir the solution until crystals begin to form.
8. Cool the flask in an ice-water mixture in a 400-mL beaker for 10 min to complete the crystallization.
9. Collect the product by gravity filtration using a 250-mL beaker to collect the filtrate. Wash the product twice with 5 mL cold water.
10. Let the aspirin dry until the next laboratory period.
11. Transfer the dried aspirin to a weighed piece of filter paper and weigh. Calculate the number of aspirin tablets you have prepared:

$$\#\text{ tablets} = \text{aspirin weight (in g)} \times \frac{15\text{ grains aspirin}}{1\text{ g aspirin}} \times \frac{1\text{ tablet aspirin}}{5\text{ grains aspirin}}$$

12. Calculate the percent yield of your aspirin from the formula below. The quantity in the denominator (2.5 g) represents the theoretical yield of aspirin based on the moles of salicylic acid and acetic anhydride used in the synthesis.

$$\%\text{ yield aspirin} = \frac{\text{weight aspirin}}{2.5\text{ g}} \times 100$$

13. Determine the qualitative purity of your aspirin in the following manner. Place 1 mL methanol in each of three separate test-tubes. Add a few crystals of the following: Test-tube 1, salicylic acid; Test-tube 2, your prepared aspirin; and Test-tube 3, commercial aspirin, crushed. Add 1 drop of 1% iron(III) chloride solution to each test-tube. Observe the color in each tube. What can you conclude?
14. Extension: Determine the melting point of the aspirin as directed by your instructor.
15. Place the aspirin in a dry test-tube, label with your name(s), and give it to your teacher.
16. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Can the purity of the prepared aspirin be determined by the color test with the iron(III) chloride?
2. Can the purity of the prepared aspirin be determined by the melting point?
3. In Step 12, the quantity 2.5 g represents the theoretical yield of aspirin. Show the calculation leading to a theoretical yield of 2.5 g of aspirin. *[You must first determine the limiting reactant from the following data: Molar mass of salicylic acid = 138 g; molar mass of acetic anhydride = 102 g; density of acetic anhydride 1.08 g/mL.]*

Implications and Applications

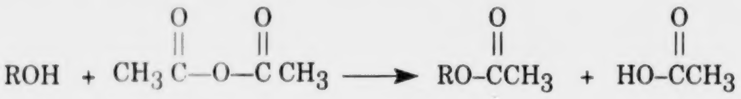
1. What steps do aspirin manufacturers have to take to make sure that their product is fit for human ingestion?
2. What other types of analgesics are on the market? How does their action compare with aspirin and why are these alternative drugs necessary?

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Synthesis of Aspirin

Major Chemical Concept

The synthesis of aspirin is known in organic chemistry as an esterification reaction. This is a substitution reaction in which an alcohol (the –OH group in salicylic acid) reacts with acetic anhydride to form an ester, aspirin.



$$\mathrm{ROH} + \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-O-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\,\mathrm{CH_3} \longrightarrow \mathrm{RO-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{HO-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$$

Level

Honor chemistry students

Expected Student Background

None expected. The techniques illustrated here (synthesis, melting point determination) are not likely to have been previously encountered.

Time

The activity will take one 50-min period for the synthesis, an overnight drying step, and a second period for calculations, color tests, and melting point determination.

Safety

Read the *Safety Considerations* in the *Student Version*. The acetic anhydride, methanol and concentrated sulfuric acid should be handled with care. Dispensing the anhydride from a buret minimizes spills and possible body contact. Concentrated sulfuric acid should be dispensed from a small dropping bottle. The aspirin produced in this activity is not pure. It is often contaminated with salicylic acid, acetic acid, and/or sulfuric acid. Students should not taste their aspirin.

Materials (For 24 students working in pairs)

Nonconsumables

- 12 Melting point devices (see *Possible Extensions*)
- Mineral oil, 1 L
- 12 Thermometers (50-150 °C)
- Capillary melting tubes
- 12 Funnels and supports
- 4 Burets, 50-mL
- 12 Erlenmeyer flasks, 250-mL
- 24 Beakers, 400-mL
- 12 Beakers, 250-mL
- 12 Graduated cylinders, 10-mL
- 12 Graduated cylinders, 50-mL
- 12 Flat-tipped spatulas or "rubber policemen"
- 12 Ring stands, rings and wire gauze
- 12 Stirring rods

Consumables

Salicylic acid, 24 g
Acetic anhydride, 60 mL
Concentrated sulfuric acid, 5 mL (in dropping bottles)
Crushed ice
Methanol, 50 mL
Commercial aspirin sample
1% Iron(III) chloride, $FeCl_3$, 100 mL (1 g $FeCl_3$ per 100 mL solution)

Advance Preparation

Fill the 50-mL buret with acetic anhydride. Prepare 1% iron(III) chloride solution in dropping bottles. Set out container of salicylic acid. Use of vacuum filtration, if available, will facilitate the filtration. Purchase commercial aspirin tablets, or obtain samples from the school health office. Set up mineral oil baths for melting point determination as shown in *Possible Extensions*.

Pre-Laboratory Discussion

1. Briefly explain the reaction type (substitution, esterification) and synthetic goal.
2. Caution students about reagent hazards.
3. Review the use of a buret for delivering a given volume of liquid.
4. Review technique of stirring versus swirling.
5. Review theoretical yield calculation.
6. Explain the concept in the iron(III) chloride test. Many phenols form colored coordination compounds with iron(III) ion, in which six molecules of a monohydric phenol are combined with one atom of iron in the form of a complex anion. Salicylic acid contains a phenolic –OH group and gives a positive test (turns purple) with iron(III) chloride. Complete reaction of salicylic acid with acetic anhydride substitutes an ester for the phenolic group. Therefore, aspirin uncontaminated with the salicylic acid starting material will give a negative test with Fe^{3+}. What can students conclude if their aspirin preparation turns purple? *[The preparation still has salicylic acid starting material present.]*
7. Explain how to obtain a melting point range (temperature at which solid first melts to the temperature at which solid is melted).

Teacher-Student Interaction

Walk around room during laboratory exercise emphasizing proper technique. Talk with students to ascertain if they understand activity. Help with yield calculations and melting point determination.

Anticipated Student Results

Typically students obtain a 60-70% yield. The product is often contaminated with salicylic acid. The result of the iron(III) chloride test is: salicylic acid (dark purple), prepared aspirin (dark purple), and commercial aspirin (light salmon). The melting point range is broad, *i.e.*, there is a large temperature range between first melting and complete melting of the sample. Typical values are between 128-137 °C. Recrystallization of the aspirin would remove unreacted salicylic acid and narrow the melting point range.

Answers to Data Analysis and Concept Development

1. Yes. The prepared aspirin should not give a positive color test with the iron(III) chloride because salicylic acid, which gives the positive test, is absent.
2. Yes. The sharpness of the melting point is one of the best methods of determining purity of an organic solid. A broad melting point indicates the presence of impurities. In this case, the impurity is probably a trace of unreacted salicylic acid.
3. The number of moles of salicylic acid used is 0.014 mol $[2.0\text{ g} \times \frac{1\text{ mol}}{138\text{ g}}]$.

   The number of moles of acetic anhydride is 0.53 mol $[5.0\text{ mL} \times 1.08\frac{\text{g}}{\text{mL}} \times \frac{1\text{ mol}}{102\text{ g}}]$.

   The theoretical amount of aspirin that can be obtained based on a balanced equation of 1 mol acetic anhydride to 1 mol of salicylic acid (the limiting reagent) is 2.5 g $[0.014\text{ mol} \times \frac{180\text{ g}}{1\text{ mol}}]$.

Answers to Implications and Applications

1. Purification by recrystallization and testing for impurities by melting point determination and chromatography are necessary. Strict regulatory codes apply.
2. Other analgesics may be anti-inflammatory or antipyretic, but only aspirin is a "triple action" drug (fulfills all three functions). Aspirin is sometimes irritating to the digestive tract lining, so alternatives must be available for individuals affected by aspirin in this way.

Post-Laboratory Discussion

Review the experimental techniques, the experimental results and their significance.

Possible Extensions

1. Determine the purity of your aspirin by obtaining its melting point. Use the set-up shown in Figure 1. Crush about 50-100 mg of dry aspirin with a spatula against the walls of a 50-mL beaker. Thrust the open end of a melting point capillary tube into the powdered aspirin several times. Work the plug of solid material down to the tube's sealed end by dropping it 3-4 times into the open end of the 50-mL beaker used for crushing. The capillary tube should contain the amount of packed solid as shown in Figure 1.

   Attach the capillary tube to the thermometer as shown in Figure 1. The rubber band can be a small section of rubber tubing of suitable diameter. Place the thermometer and tube in the 250-mL beaker oil bath. Heat the oil bath so that the temperature rises about 1-2 °C/min. Record as the melting point range the temperature at which the sample begins to melt and the temperature at which the sample is completely melted. The melting point of aspirin is about 135 °C. Discard the used melting point tubes in a waste glass container.

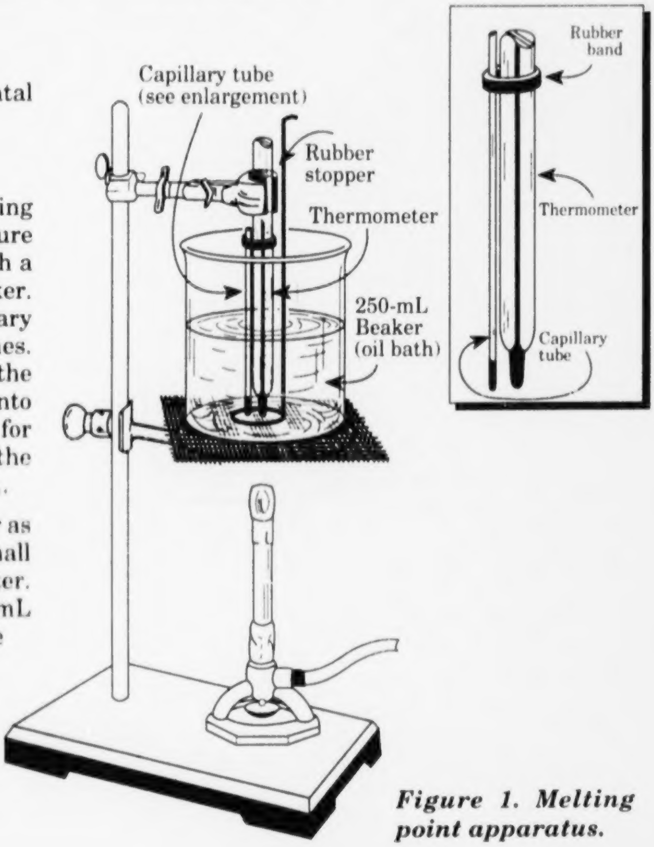
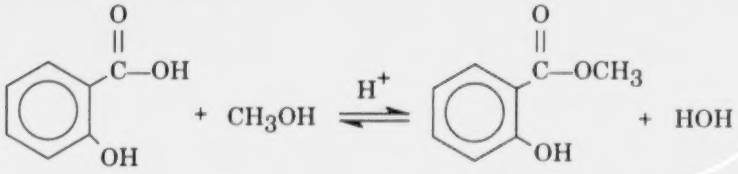


Figure 1. Melting point apparatus.

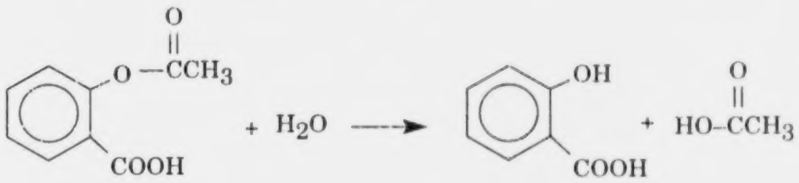
2. Synthesize methyl salicylate (oil of wintergreen) in a medium-sized test-tube from 0.5 g salicylic acid and 1 mL methanol. Stir the mixture, and add 3 drops of concentrated sulfuric acid. Heat the mixture in a water bath for 5 min. Remove the test-tube, cool it in a test-tube rack, and then add the contents to a 100-mL beaker containing 4-5 ice cubes. Waft the odor toward the nose. What commercial products contain oil of wintergreen? *[Wintergreen Life-Savers, Ben-Gay,* etc.*]*



3. Use a Spectronic 20 to determine the amount of salicylic acid in the laboratory-synthesized aspirin and in commercial aspirin. To prepare an aspirin solution, dissolve 0.05 g aspirin in 50 mL water. Prepare an iron(III) nitrate solution by dissolving 2 g iron(III) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9\ H_2O$] in 50 mL water and adding 0.5 mL concentrated nitric acid. To 1 mL aspirin solution add 5 mL iron(III) nitrate solution. Shake well for 5 min (a violet color should appear if salicylic acid is present). Measure the absorbance at 535–540 nm by placing the violet solution in the cell of a Spectronic 20 instrument after standardizing with distilled H_2O. *NOTE:* Old Spectronic 20's may still have their wavelength scales calibrated in mμ (millimicrons) but the accepted term for this unit is nanometers(nm). The absorbance is proportional to the concentration of salicylic acid in the sample. Compare your laboratory aspirin with several brands of commercial aspirin. *[The laboratory synthesized aspirin should have an absorbance >0.5 at 540 nm. The commercial aspirin has an absorbance of <0.2 at 540 nm. The commercial aspirin solution does not change to a violet color when mixed with the iron(III) nitrate solution.]*

Assessing Laboratory Learning

1. What are the most likely impurities present in the sample of aspirin you prepared? *[Unreacted salicylic acid, traces of acetic acid.]*
2. If aspirin sits for long periods of time, the odor of vinegar can be noticed in the container. A hydrolysis reaction occurs very slowly. Explain, using a chemical equation, the source of the vinegar, and the reason for the hydrolysis. *[Slow reaction with moisture in air can produce small amounts of vinegar.]*



3. A white powder was tested by a police chemist with iron(III) chloride solution. A purple color is seen. What conclusion was drawn by the police chemist? *[The white powder contained a phenolic compound, possibly salicylic acid.]*
4. Aspirin tablets are sold as containing 5 grains of aspirin. If 1 grain equals 65 mg, how many milligrams of aspirin does each tablet contain? *[325 mg]*

DEMONSTRATIONS

CAUTION: Use appropriate safety guidelines in performing demonstrations.

Demonstration 1: Reaction in a Breathalyzer

Purpose

The chemistry of some Breathalyzers involves the reduction of orange chromium(VI) to green chromium(III) by ethanol. In this activity, an orange solution of chromium(VI) is added to four quadrants of a Petri dish. Ethanol is then added to one quadrant until a color change occurs. Differing amounts of ethanol are added to the second and third quadrants, and the color changes are compared to each other and to the standard (control). (*NOTE: Most Breathalyzers used by law enforcement agencies now utilize infrared analysis.*)

Materials

4-Quadrant glass Petri dish (or four separate dishes arranged in a square)
Overhead projector
Stirring rod
3 Medicine droppers
Paper towel
Chromic acid reagent [add 6 g chromium(VI) oxide (CrO_3) to 12 mL concentrated sulfuric acid and stir until a smooth paste is obtained.

Cautiously dilute the paste with 40 mL distilled water, and stir until a clear orange solution is obtained. Cool to room temperature.]

Ethanol, 45% [47 mL 95% ethanol (C_2H_5OH) per 100 mL solution]

Safety

Handle the chromic acid solution with care. It is a strong oxidizing agent, toxic by ingestion, and an alleged carcinogen. Follow proper disposal procedure (see *SourceBook Safety* section and your local requirements for disposal).

Procedure

1. Place the Petri dish on the overhead projector with the lamp on (or on a white sheet of paper on the desktop).
2. Add 15 drops chromic acid solution to each quadrant in the Petri dish. Add 15 drops distilled water to each quadrant and mix.
3. Keep Quadrant 1 as a control.
4. Add 1 drop 45% ethanol to Quadrant 2.
5. Add 2 drops 45% ethanol to Quadrant 3.
6. Add 3 drops 45% ethanol to Quadrant 4.
7. Compare the intensity of the green-brown color produced in each quadrant as a function of the amount of ethanol added. Make observations after 1-2 min. *[Quadrant 2 contains a light colored precipitate; Quadrant 3, medium-dark; and Quadrant 4, a heavy dark precipitate. The increasing amount of precipitate indicates the increasing amount of ethanol oxidized.]*

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. Is water a drug? *[When given therapeutically to a dehydrated person, water can be considered a drug.]*
2. Under what condition might aspirin not be considered a drug? *[When taken by an anxious insomniac, aspirin would have no drug effect.]*
3. Using the four names for a common drug given here, identify the generic name, the street name, the chemical name, and the brand name: blue birds, sodium pentobarbital, sodium 5-ethyl-5-(1-methylbutyl) barbiturate, Nembutal. *[Generic name: sodium pentobarbital; street name: blue birds; chemical name: sodium 5-ethyl-5-(1-methylbutyl) barbiturate; brand name: Nembutal.]*
4. A patient purchases a cough syrup consisting of 200 mL liquid. The label directs the patient to take 1 teaspoonful four times a day. How long will the prescription last if 1 teaspoon is equivalent to 5 mL? *[10 days]*
5. If the usual dose of a sulfa drug for a urinary tract infection is 2.00 g/kg body weight, how many grams of the drug should be given to a female if she weighs 120 lb (2.20 lb = 1 kg)? *[109 g]*
6. Examine the labels of three combination pain relievers (Bufferin, Excedrin, Vanquish, *etc.*). Make a list of the ingredients of each. Look up the medical uses, dosages, side effects, and toxicities of each in *The Merck Index*.

Counterintuitive Examples and Discrepant Events

1. "My tooth stopped hurting when I got to the dentist's office" or "Doctor, I feel better just because you are here." The anticipation of professional help is often reassuring to patients and provides support. It has much the same effect as a placebo. It is believed that certain natural body (endogenous) drugs (endorphins, adrenal hormones, and neurotransmitters) are released in this clinical and verbal approach.
2. Methanol (methyl alcohol) poisoning is treated by intravenous injection of ethanol (ethyl alcohol). Ethanol is oxidized more easily by the enzyme that catalyzes the oxidation of methanol in the body, and methanol is excreted unchanged in the urine. Enzyme oxidation of methanol yields formaldehyde and formic acid, both highly toxic substances. By saturating the system with ethanol, methanol cannot compete successfully for the enzyme and will be excreted largely unchanged.
3. More is better (a vitamin ad). Ingestion of large dosages of vitamins have been touted as being highly beneficial. Linus Pauling, twice winner of the Nobel Prize, advocates large daily doses of Vitamin C. While the beneficial effects of this practice remain in doubt, at least it should do no harm since Vitamin C is water soluble and will be quickly excreted. The fat-soluble vitamins, however, are not so quickly excreted and can end up in the body's fat reserves. Thus, overdosages of fat-soluble vitamins (*e.g.*, Vitamin A) have been documented in the medical literature and can lead to serious problems, even death.

Pictures in the Mind

1. TV Public Service message: "This is your brain (an egg); this is your brain on drugs (egg on a hot grill)."

2. TV Public Service message: "Before you get on drugs, you'd better know what you're jumping into (diver plunges into an empty swimming pool)."

TIPS FOR THE TEACHER

Language of Chemistry

1. Classification of drugs.

Designation	Examples	Description
Controlled substances		Substances whose sale, distribution, and possession is controlled by the Drug Enforcement Administration
Schedule 1	Heroin, LSD, mescaline	Abused drugs with no medical use
Schedule 2	Morphine, amphetamines	Abused drugs with medical uses
Schedule 3	Valium, phenobarbital	Prescription drugs that are often abused
Over-the-Counter (OTC)	Antacids, aspirin, cough medicines	Available to anyone
Prescription drugs	Antibiotics	Available only by prescription
Unregulated nonmedical drugs	Ethanol, caffeine, nicotine	Available in beverages, foods, or tobacco

Figure 2. Drug classifications.

2. Addiction, dependence, and tolerance are three terms used in describing the effects of some substances. **Addiction** is the continued need of a substance to function normally and to prevent the occurrence of withdrawal symptoms. **Dependence** is experience of withdrawal symptoms if use of the substance stops. **Tolerance** is the need for increasing amounts of a substance to experience the desired effect.

3. **Chemotherapy** is a planned attack on a disease using a specific chemical. Such substances have been designed to attack the disease center (not just relieve the symptoms), do their job and not harm healthy tissue. Substances have been prepared for that very purpose (see also Drug Design in *Links and Connections* section). Some chemotherapeutic agents and the disease they attack are: Salvarsan, syphilis; antibiotics, bacterial infections; radioactive iodine, thyroid cancer; and antimetabolites, some cancers. The possibility of side effects from the use of chemotherapy is a major problem.

4. An **antacid** is an alkaline substance that reacts with excess stomach acid (HCl). As shown in Figure 3, there are many varieties of over-the-counter (OTC) antacids. The most common antacid ingredients are sodium bicarbonate ($NaHCO_3$), calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), aluminum hydroxide ($Al(OH)_3$), and magnesium hydroxide ($Mg(OH)_2$). The carbonate antacids neutralize excess hydrochloric acid with the liberation of CO_2.

$$HCO_3^-(aq) + HCl(aq) \rightarrow Cl^-(aq) + H_2O(l) + CO_2(g)$$

or

$$CO_3^{2-}(aq) + 2HCl(aq) \rightarrow 2Cl^-(aq) + H_2O(l) + CO_2(g)$$

Product name	Antacid ingredients
Alka 2	$CaCO_3$
Alka-Seltzer Blue[a]	$NaHCO_3$ + Citric acid
Alka-Seltzer Gold	$NaHCO_3$ + Citric acid
Amitone	$CaCO_3$
Bisodol	$NaHCO_3$ + $MgCO_3$
Bisodol (low sodium)	$Mg(OH)_2$ + $CaCO_3$
Brioschi	$NaHCO_3$ + Tartaric acid
Bromo-Seltzer[b]	$NaHCO_3$ + Citric acid
Camalox	$Mg(OH)_2$ + $Al(OH)_3$ + $CaCO_3$
Creamalin	$Mg(OH)_2$ + $Al(OH)_3$
Di-Gel[c]	$Mg(OH)_2$ + $Al(OH)_3$
Eno	Na Tartrate + Na Citrate
Gelusil[c]	$Mg_2Si_3O_8$ + $Al(OH)_3$
Maalox	$Mg(OH)_2$ + $Al(OH)_3$
Milk of Magnesia	$Mg(OH)_2$
Mylanta[c]	$Mg(OH)_2$ + $Al(OH)_3$
Rolaids	$NaAl(OH)_2CO_3$
Titrilac	$CaCO_3$
Tums	$CaCO_3$

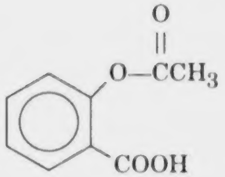
[a] Contains aspirin

[b] Contains acetaminophen

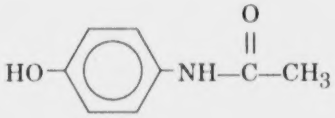
[c] Contains a silicone defoaming agent

Figure 3. Popular commercial antacid products.

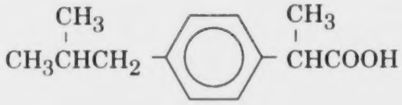
5. **Analgesics** (pain relievers) in common use today are aspirin, acetaminophen, and ibuprofen. All are available as over-the-counter (OTC) preparations. Of the three, aspirin is the only analgesic (reduces pain), antipyretic (reduces fever), and anti-inflammatory (reduces swelling). Acetaminophen is both an analgesic and antipyretic. Acetaminophen has been used as a combination pain reliever with codeine. Ibuprofen is an analgesic. The structure of each is shown below:



Acetylsalicylic acid (aspirin)



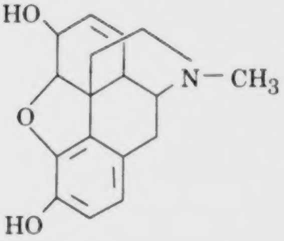
Acetaminophen



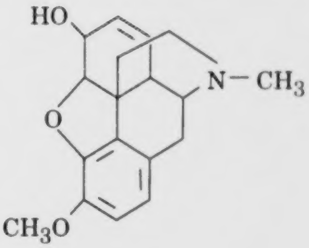
Ibuprofen

Typical doses of aspirin and acetaminophen are 325 mg and for ibuprofen, 200 mg. These drugs have drawbacks. Aspirin causes intestinal bleeding and may cause allergies. It has been implicated in Reye's syndrome, a life-threatening condition that may follow flu or chicken pox in children and teenagers. Acetaminophen is not useful to patients with arthritis, and it is toxic to the liver in large doses. Ibuprofen causes intestinal bleeding and impairs kidney function.

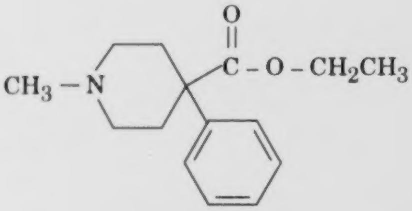
6. **Narcotic analgesics** are used to obtain higher levels of pain relief (*e.g.*, the pain associated with fractures, kidney stones, heart attack, gallstones) than can be achieved with the OTC aids. They produce stupor or insensibility as well as addiction and withdrawal symptoms and increasing tolerance. Narcotic analgesics include codeine, morphine, and meperidine (Demerol™). Morphine is found naturally in the opium poppy. Codeine is made by methylating (substituting the CH_3– group for H–) morphine. Meperidine is a synthetic narcotic. The dose for pain relief of these analgesics is typically 5–120 mg.



Morphine



Codeine



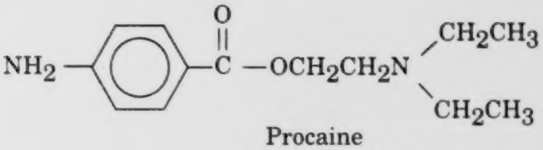
Meperidine
Demerol®

7. **Combination pain relievers** contain aspirin and caffeine. Caffeine is a mild stimulant found in coffee, tea, and cola drinks. Evidence indicates that caffeine counteracts the action of aspirin. Thus combination pain relievers containing caffeine are less effective. Some combination pain relievers contain an antacid.

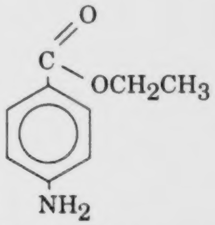
8. Colds are caused by viruses, and antibiotics are not effective against cold viruses. **Cold remedies** treat only the symptoms and may contain a cough suppressant, a nasal decongestant, and an antihistamine. The cough suppressant is either codeine or dextromethorphan. The antihistamine, usually diphenhydramine or chlorpheniramine, relieves allergy symptoms (sneezing, itchy eyes, and runny nose). The nasal decongestants are usually ephedrine and phenylephrine. These drugs have been found to be safe and effective when taken as directed, but antihistamines can cause drowsiness and are potentially hazardous to anyone who needs to be alert. Abuse of cold remedies can lead to addiction.

9. Some well-known combination remedies are shown in Figure 4.

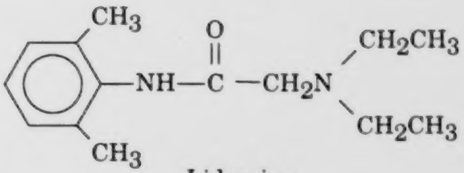
10. **Local anesthetics** render one part of the body insensitive to pain. Benzocaine is available in some OTC preparations for localized surface pain and itching. Procaine and lidocaine are more potent and are used in dental repair or for minor surgery.



Procaine
(Novocain®)



Ethyl *p*-aminobenzoate
(Benzocaine)



Lidocaine
(Xylocaine®)

Product name	INGREDIENTS				
	Analgesic	Antacid	Antihistamine	Decongestant	Other
Akla-Seltzer (Blue)	Aspirin	$NaHCO_3$			Citric acid[a]
Alka-Seltzer Plus	Aspirin	$NaHCO_3$	Chlorpheniramine	Phenylpropanolamine	Citric acid[a]
Allerest			Chlorpheniramine	Phenylpropanolamine	
Anacin	Aspirin				Caffeine
Arthritis Pain Formula	Aspirin	$Al(OH)_3$ $Mg(OH)_2$			
Bufferin	Aspirin	$MgCO_3$ aluminum glycinate			
Comtrex	Acetaminophen		Chlorpheniramine	Pseudoephedrine	Dextromethorphan[b]
Contac			Chlorpheniramine	Phenylpropanolamine	Belladonna Alkaloids Caffeine
Cope	Aspirin	$Al(OH)_3$ $Mg(OH)_2$			
Coricidin	Aspirin		Chlorpheniramine		
Coricidin D	Aspirin		Chlorpheniramine	Phenylpropanolamine	
CoTylenol	Acetaminophen		Chlorpheniramine	Phenylpropanolamine	Dextromethorphan[b]
Day Care	Acetaminophen			Phenylpropanolamine	Dextromethorphan[b] Alcohol (7.5%)
Dristan	Aspirin		Chlorpheniramine	Phenylephrine	Caffeine
Empirin	Aspirin, Phenacetin				Caffeine
Excedrin	Aspirin, Salicylamide, Acetaminophen		Pyrilamine[c]		Caffeine
NyQuil	Acetaminophen		Doxylamine	Ephedrine	Dextromethorphan[b], alcohol (25%)
Vanquish	Aspirin, Acetaminophen	$Al(OH)_3$ $Mg(OH)_2$			Caffeine[b]

[a] Causes effervescent action.

[b] Cough suppressant.

[c] Found in Excedrin PM only.

Figure 4. Some well-known combination remedies.

11. **Antiseptics** are compounds that are applied to living tissue to kill microorganisms or to prevent their growth. Many are mild oxidizing agents and are effective because they oxidize bacterial cells (as well as human cells) or weaken cell walls so that the cell contents cannot be contained (see Figure 5).

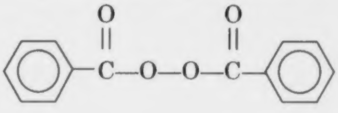
Antiseptic	Concentration	Use
1. Hydrogen peroxide	3%	Topical antiseptic
2. Potassium permanganate	0.01–0.2%	Topical antiseptic, astringent
3. Benzoyl peroxide	5–10%	Acne ointments
4. Isopropyl alcohol	70%	Rubbing alcohol
5. Quaternary ammonium compounds	—	Surface-active agents
6. Iodophors (iodine + polyvinylpyrrolidone complex)	—	Restaurant glassware
7. Hexylresorcinol	—	Antiseptic

H_2O_2

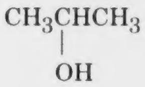
(1)

$KMnO_4$

(2)

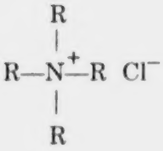


(3)



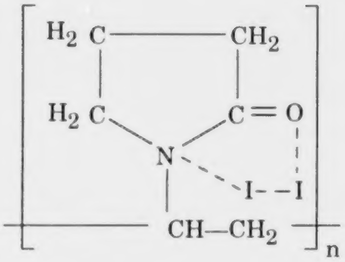
$CH_3CH(OH)CH_3$

(4)



$R_4N^+ Cl^-$

(5)



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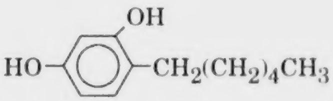
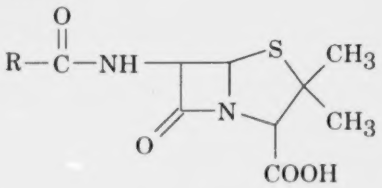


(7)

Figure 5. Some common antiseptics.

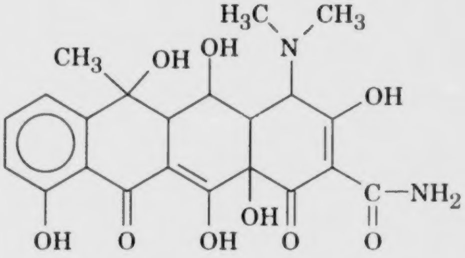
12. **Vitamins** are organic compounds required in small amounts in the diet because they cannot be synthesized by the body. Lack of proper amounts of vitamins in the diet can lead to vitamin-deficiency diseases. For example, Vitamin A deficiency leads to nightblindness (poor vision in dim light), Vitamin D deficiency lead to rickets (soft and poorly mineralized bones), and Vitamin K deficiency leads to hemorrhaging. Some vitamins are necessary in making certain coenzymes. For example, riboflavin is needed for flavin adenine dinucleotide (FAD), and niacin is needed for nicotinamide adenine dinucleotide (NAD). These particular coenzymes are involved in oxidation-reduction reactions. Megadoses of vitamins, unless prescribed by a physician, are dangerous.

13. **Antibiotics** are derived from molds or bacteria and inhibit the growth of other microorganisms. Discovered in 1941, penicillin is made by the mold *Penicillium notatum*. Many different penicillins exist, differing only in the structure of the R group in the general formula shown below. The nature of the R group determines whether or not the penicillin can be taken orally or by injection, and whether it causes diarrhea or an allergic reaction.



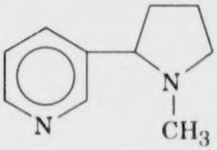
Penicillin

Tetracycline antibiotics get their name from their four-ring structure. First used in 1950, they are effective against a wide variety of microorganisms. Initially obtained from fungi, many tetracyclines are synthesized today. Terramycin is a typical example.



Terramycin

14. **Nicotine** and Smoking. People smoke for enjoyment, to alleviate stress, or because they are addicted to nicotine. Yet nicotine, the active ingredient in tobacco, is toxic. It is lethal at doses of about 60 mg, and a typical cigar contains at least 120 mg. However, only about 10% of that amount is absorbed on inhaling the smoke, and over a relatively long period. A typical filter cigarette contains 20-30 mg of nicotine. Low doses of nicotine increase respiratory rate, stimulate an increased heart rate and blood flow, and constrict the arteries. Regular smokers exhibit a shortness of breath because CO and HCN formed in the combustion processes bind to hemoglobin, diminishing its ability to carry oxygen. At high doses, nicotine interferes with nerve impulse transmission. Tolerance can be developed for small amounts of nicotine along with a dependency.

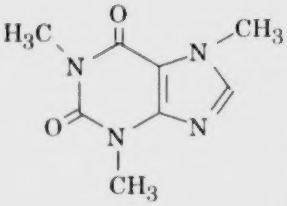


Nicotine

It is not just the nicotine in cigarettes that is harmful. Benzpyrene, found in tobacco smoke, is an extremely carcinogenic compound. Tobacco also contains β-naphthylamine, which causes bladder cancer.

Individuals chewing or dipping smokeless tobacco have a particularly dangerous habit. Smokeless tobacco causes tooth decay (it has a high sugar content), gum disease, and oral cancer. Nicotine levels in the blood of smokeless tobacco users is comparable to or greater than cigarette smokers.

15. **Caffeine** is found in tea, coffee, and cola drinks. Caffeine is an **alkaloid** (*i.e.*, can be extracted from its natural source by acid) and a stimulant. It causes an increased alertness, the ability to put off sleep, and an increased capacity for thinking, but coordination and timing may be adversely affected. It is the main ingredient in certain OTC products, such as No-Doz (100 mg caffeine per dose) and Vivarin (200 mg per dose). Caffeine users can develop tolerance and dependency. Coffee drinkers (90 mg/cup) will experience lethargy, headache, or nausea after abstaining for up to 15 hr. Cola drinkers (43 mg/can) and tea drinkers (50 mg/cup) can also experience these reactions.



Caffeine

16. **Ethanol**. Alcohol is a term that describes a class of organic compounds with a hydroxy group (–OH) bonded to a carbon atom. It is also a term that the populace uses to identify liquors, beers and wines. The alcohol contained in these and other alcoholic beverages is ethanol (CH_3CH_2OH). Beer is usually 6% ethanol by volume; wines, 12%; and 80 proof whisky, 40%. (Proof = 2 x alcohol content by volume.) Ethanol is a mild depressant slowing down physical and mental activity in moderate amounts. In very large amounts, it produces unconsciousness or death. Although alcohol's effects vary among individuals, usual effects are summarized in Figure 6. The relationship applies to a 70 kg (154-lb male) who rapidly consumes 30-mL (1-oz) shots of 90-proof (45% ethanol) whiskey.

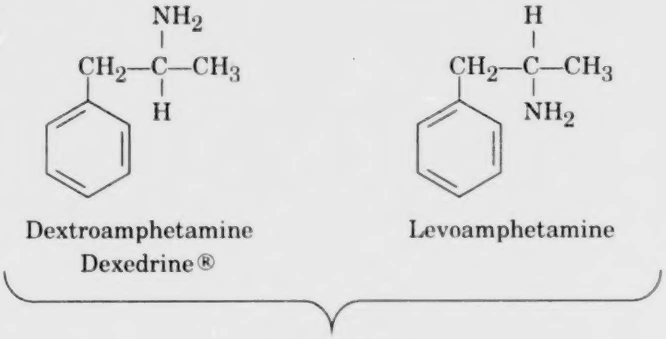
Approximate Relationship between Drinks Consumed, Blood-Alcohol Level (BAL), and Behavior

Number of Drinks	BAL (Volume %)	Behavior
2	0.05	Mild sedation; tranquility
4	0.10	Lack of coordination
6	0.15	Obvious intoxication
10	0.30	Unconsciousness
20	0.50	Possible death

Figure 6. Effects of alcohol.

Ethyl alcohol is detoxified by a liver enzyme through an oxidation reaction. In individuals who develop tolerance for alcohol, increasing amounts of the enzyme build up in the liver enabling large amounts of alcohol to be detoxified.

17. Benzedrine is a mixture of two optical isomers of **amphetamine**. These two isomers differ in the way they rotate plane polarized light. These isomers occur because of the four different groups ($C_6H_5CH_2$–, NH_2–, CH_3–, and H–) around the central carbon atom. Dexedrine is the stronger stimulant of the two. Amphetamines are central nervous system stimulants that increase heart rate and blood pressure. They increase wakefulness, drive, and energy. They produce a temporary elevation of mood, usually followed by fatigue, irritability, and depression. Users often must take barbiturates to sleep. Amphetamines have been used for weight reduction and to relieve mild depression. In colloquial language, amphetamines are called "uppers."

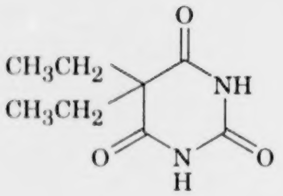


Dextroamphetamine
Dexedrine®

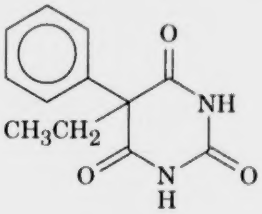
Levoamphetamine

Amphetamine
Benzedrine ®

18. **Barbiturates**, colloquially called "downers," are used to produce mild sedation (a few milligrams) and to induce sleep (about 100 mg). They are the major ingredient in sleeping pills and can cause death in the case of an overdose. Barbiturates are addictive. Users generally develop a tolerance and require larger doses to obtain the desired degree of sedation. Structurally, barbiturates are amides. Barbiturates are particularly dangerous when used along with alcohol. Both substances are depressants, but when used together the sum of the effects is magnified (synergism). The structures of common barbiturates are given to the left.

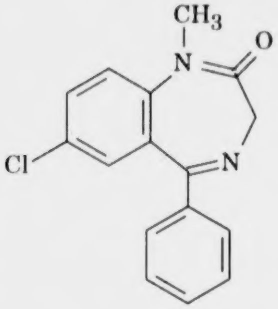


Barbital
Veronal®

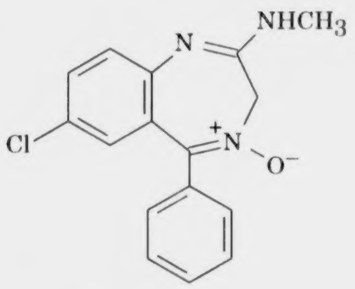


Phenobarbital
Luminal®

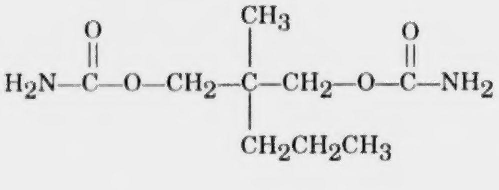
19. **Tranquilizers** are used to calm nerves and relieve tension. Cope, Vanquish, and Compoz are OTC drugs available to help individuals "cope" with problems and unwind. These products also contain aspirin and an antihistamine, which typically causes drowsiness. Tranquilizers are also available by prescription (for example, Equanil, Valium, and Librium). Many tranquilizers are addictive and attempts to stop using them have caused withdrawal symptoms. More potent tranquilizers (*e.g.*, thorazine) are useful in treating severe forms of mental illness and schizophrenia. The structure of some common tranquilizers are given.



Diazepam
Valium ®

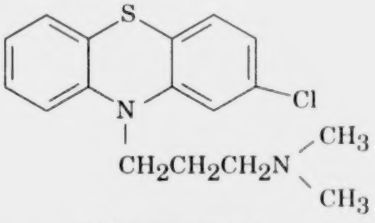


Chlordiazepoxide
Librium ®



$$H_2N-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_2CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$$

Meprobamate
Miltown®; Equanil ®



Chlorpromazine
Thorazine ®
(as hydrochloride)

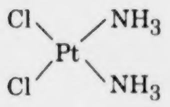
20. **Radiopharmaceuticals**. Radioisotopes are used for therapy and diagnosis in medicine. As a diagnostic tool, they provide information about the type or extent of illness. The therapeutic use is intended to treat or cure a disease. Some examples are shown in Figure 7.

Isotope	Use
Barium-131	Detection of bone tumors
Cobalt-58	Determination of uptake of Vitamin B-12
Iodine-131	Detection of thyroid malfunction, treatment of thyroid cancer
Cobalt-60	Treatment of cancer
Radium-226	Treatment of cancer

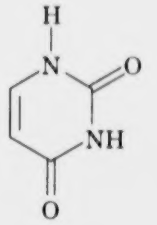
Figure 7. Some common radioisotopes and their uses.

Both diagnostic and therapeutic radioisotopes typically produce gamma radiation. In low doses, gamma radiation is less harmful to tissues than alpha or beta radiation. Although alpha and beta radiation produce more cell deaths per unit of exposure than gamma radiation, the penetrating power and ranges of alpha and beta radiation are very small. Gamma radiation penetrates tissues very effectively and, in high dosages, is very effective in causing cell death, particularly in rapidly multiplying cells. For this reason, gamma radiation is used for therapeutic purposes as well. Typically a beta emitter like cobalt-60 is used for cancer treatment. An atom of cobalt-60 transmutes to a highly excited atom of nickel-60, which emits two high-energy gamma rays in quick succession. These gamma rays have been found to be effective in the treatment of some types of cancer.

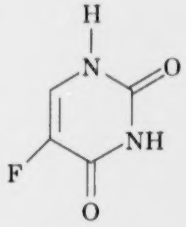
21. **Anticancer Drugs**. Cancer is cell multiplication without restraint with invasion of nearby tissue. In addition to surgical removal of affected areas and irradiation to kill the cancer cells, cancers are treated by chemotherapy use of chemical substances to kill cancer cells. These substances include alkylating agents, cisplatin, and antimetabolites. Alkylating agents are organic compounds that transfer alkylating groups to nitrogen bases (usually guanine) in DNA. The presence of the alkyl group in guanine prevents DNA replication (and thus, cell division). Cisplatin also blocks DNA replication. Antimetabolites interfere with synthesis of a nucleotide necessary for DNA synthesis and therefore inhibit cell division. 5-Fluorouracil is an antimetabolite (see Drug Design in *Links and Connections* section). The use of these substances is based on the premise that cancer cells are undergoing rapid division and will be affected to a greater extent than healthy cells. In the long run, healthy cells suffer as well. Chemotherapy has provided an improvement in patient survival with some cancers, particularly breast, bladder, and colon cancer, and Hodgkin's disease.



Cisplatin

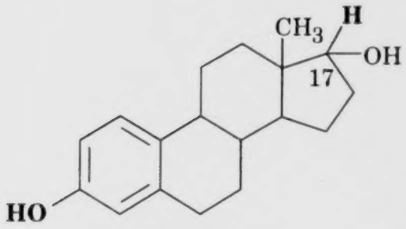


Uracil

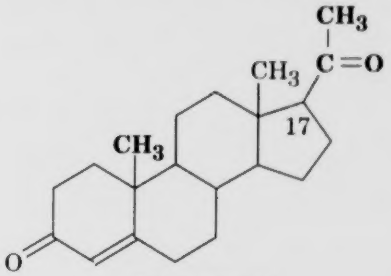


5-Fluorouracil

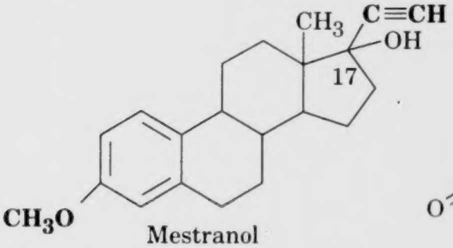
22. **Birth control pills** are steroids inhibiting ovulation and "convincing" the body that it is pregnant. If an egg is not released, females cannot become pregnant. The pill, a synthetic hormone-like substance, was first used in 1960. For most females the pill is safe, but some women experience undesirable side effects: hypertension, acne, and abnormal bleeding. A combination pill that contains both synthetic estrogen and progesterone is typically used. Notice the structural similarity of these synthetic compounds (mestranol and norethindrone) to the female sex hormones progesterone and estradiol. Substitution of the $-C{\equiv}CH$ group for a $-CH_3$ group at C-17 allows for a more effective drug (see *Drug Design* in *Links and Connections* section).



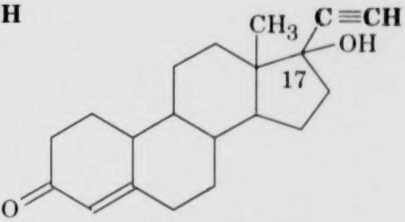
Estradiol



Progesterone

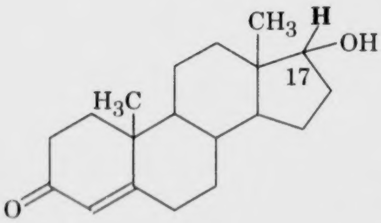


Mestranol

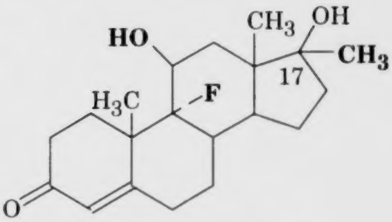


Norethindrone

23. **Anabolic steroids** are synthetic derivatives of testosterone. These drugs are used in therapy to correct hormonal imbalance or to prevent withering of muscle in persons who are recovering from surgery or starvation. Healthy athletes use these drugs in doses 10 times the therapeutic dose to build muscle mass. When so used, a number of side effects are noticed including acne, baldness, enlargement of the breasts, and changes in sexual desire. In women, use of anabolic steroids produces facial hair, deepening of the voice, and changes in the menstrual cycle. Anabolic steroids are toxic to the liver. Notice the structural relationship between testosterone and fluoxymesterone, a typical anabolic steroid. The presence of the $-CH_3$ group at C-17 is thought to slow the metabolism of the steroid in the liver and increases liver toxicity.



Testosterone



Fluoxymesterone

24. The following reference guide to some drugs that are subject to abuse is available from Council on Drug Abuse, 698 Weston Road, Toronto, Ontario, M6N 3R3; (416) 763-1491.

DRUG EFFECTS...the important effects are the ones that you don't feel.

What a drug does to the mind, body or both depends on much more than simply the drug the person is taking, including the following:

1. **How big you are.**
2. **How old you are.**
3. **Your mood and emotions at the time you take it.**
4. **How much you take.**
5. **How strong the drug is.**
6. **How fast you take it.**
7. **How it gets into the body, (eating, smoking, *etc.*)**
8. **Your general physical condition.**
9. **What other drugs are in your body at the time.**
10. **What is already in your stomach.**

ALCOHOL

EXAMPLES

Wine
Beer
Distilled Spirits (Rye, Scotch, Rum, Vodka and Liqueurs)

MAJOR DANGERS

Whatever the word "alcoholic" means, some people keep using alcohol even when it is killing them. Drinking impairs decision-making and control of muscles, leading to increased risks of car accidents, fighting, violence and suicide. Alcohol often makes people do things they know are wrong, or do not believe in. These problems can occur even when the drinker does not feel drunk. People may die from overdose if they drink too much too fast, or if they mix alcohol with other drugs such as sleeping pills. Overdose kills people by making them unconscious and then stopping their breathing. Any person, including a teenager, who drinks can develop alcoholism. Heavy alcohol use is likely to lead to problems at work, at school, and in the family. It can also result in bankruptcy, crime and foolish gambling. Some individuals have committed murder under the influence of alcohol. Alcohol can permanently damage the brain and the liver. It helps cause heart attacks, cancer of the throat or the stomach, and other diseases. Pregnant women should not drink alcoholic beverages without seeking advice from a physician.

CLASSIFICATION

Alcohol in any form is a depressant. A depressant slows everything down and can cause people to fall asleep, or stop breathing.

MEDICAL USES

There aren't many medical uses for alcohol. Ask your doctor for advice.

LEGAL OFFENSES

There are many: such as buying it from the wrong place, drinking under age, having it in the wrong place, being drunk in public and giving it to people who are too young to have it legally and so on. The law varies from one state to another.

SLANG NAMES

"Booze"
"Sauce"
"Juice"

SYMPTOMS and BEHAVIORS

Wine, beer, rye and all other alcoholic beverages have the same effect on your body, and what alcohol does depends on how much you drink, how big you are, how old you are and how fast you drink. You can have heartburn, vomiting and dizziness. Alcohol can take away some of the benefits of eating proper food. Alcohol effects include making people feel angry, uptight, or itching for a fight. With frequent drinking, tolerance develops, which means it takes more alcohol to produce the same effect. This is the main reason why some people drink a lot without showing signs of being drunk. However, such people are still impaired because the brain does not develop much tolerance.

HALLUCINOGENS (1)

EXAMPLES

LSD
DMT
DET
STP (DOM)
Psilocybin ("Magic Mushrooms")
Mescaline
Peyote

MAJOR DANGERS

Hallucinogen users may see or hear things that aren't there. Nobody can predict how long these effects will last. Users do not know what they will do or how they will feel when hallucinogens are used, even if used before. Users may think they cannot be hurt so they may try to stop a speeding car or step off a roof. Occasionally people have been known to kill themselves or other people while under the influence of these drugs. "Flashback" or "afterflash" can happen months after the last time users took the drug—this means that they go on a "trip" again without taking the drug again.

CLASSIFICATION

They can speed up the body's workings and/or slow them down.

MEDICAL USES

None

LEGAL OFFENSES

Having it, selling it, having enough of it that the court thinks that you intended to sell it.

SLANG NAMES

"Acid"
"Blotters"
"Cids"
"Micro Dots"
"Shrooms"
"Window Panes"
"Double Domes"
"Orange Sunshine"

SYMPTOMS and BEHAVIORS

Nobody can predict what these drugs will do to users. Generally, however, users may seem very happy, very depressed, angry or terrified, restless, see things that are not there, talk to people who aren't there; colors and shapes may change. Users may vomit, or get the shakes or start sweating. The difference between what is real and what is not may not be known.

HALLUCINOGENS (2)

EXAMPLES

Cannabis
Marijuana
Hashish
Hash oil
Marijuana oil

MAJOR DANGERS

Just before, during, and after feeling high, users usually cannot tell how far away something is or how fast it is coming. Usually users cannot tell if there is any crisis to react to. For both these reasons operating any kind of a machine can be very dangerous—including bikes, cars, punch presses, swings, sleds and skateboards. Marijuana cigarettes have been rated from 5 to 22 times worse for the lungs than tobacco. Regular users may be less able to fight off infections from viruses and bacteria. The chemicals from cannabis stay in the body for a long time. They may cause birth defects or interfere with sexual activity. Regular users often fail at their work or school; they lose interest in many things. Cannabis affects memory and limits the user's ability to concentrate. Most users take other drugs. They can do many things that they know are wrong or just not their way, such as stealing or lying. Tolerance develops with regular use, and the user needs more to get the same effect. The drug itself may not cause permanent brain damage, but it can permanently change your life, for example, by causing you to fail in school.

CLASSIFICATION

It can speed up the body's workings and slow them down. With high doses, it may work as a hallucinogen (user sees and hears things that are not there).

MEDICAL USES

No widely accepted uses.

LEGAL OFFENSES

Having it, selling it, having enough of it that the court thinks that you intended to sell it, sending it, lending it, offering to sell it.

SLANG NAMES

"Pot"
"Grass"
"Weed"
"Smoke"
"Hash"
"Honey Oil"
"Thai Stick"
"Colombian"
"Ganja"

SYMPTOMS and BEHAVIORS

Cannabis drugs can give users red eyes, severe coughs, and shortness of breath. Regular use in the long term can produce lung diseases like bronchitis, cancer, and emphysema (a lung disease that cannot be cured). When high, the user can be dreamy, talkative, or laugh a lot. Mood changes very rapidly and the user often cannot remember what happened a few minutes ago. If used often, the user may drop out of activities and become less interested in many things—including the future.

HALLUCINOGENS (3)

EXAMPLES

PCP (Phencyclidine)

MAJOR DANGERS

The people who sell this drug tell the customer that it is THC, LSD, or something else. Like most hallucinogens, this drug is unpredictable. What usually happens is users cannot feel pain, and this is dangerous. Users have died from accidental overdose or from getting into situations where they were killed in a fight. In some cases suicide can result. There is probably permanent brain damage from the use of PCP. It is especially dangerous, like most drugs, when mixed with any other drug. The other dangers are the same as those listed above for LSD.

CLASSIFICATION

It can speed up the body's workings and/or slow them down. It is an hallucinogen, which means that the user may see and hear things that aren't there.

MEDICAL USES

None

LEGAL OFFENSES

Having it, selling it, having enough of it that the court thinks that you intended to sell it, sending it, lending it, offering to sell it..

SLANG NAMES

"Hog"
"Dust"
"Angel Dust"

SYMPTOMS and BEHAVIORS

There is no telling how someone will react on PCP. It is known that blood pressure increases dramatically, and users can stay up for several days. PCP can act like alcohol, marijuana, LSD or all of these. Users are confused, see or hear things that are not there, and may have convulsions and can fall into a coma.

NARCOTICS

EXAMPLES

From Opium:

- Heroin
- Morphine
- Codeine

Synthetic:

- Methadone
- Demerol
- Percodan
- Talwin

MAJOR DANGERS

Many users get quickly and severely addicted. The narcotic addict stops caring about self, work or other people. Those who use a needle can get infections, blood diseases, and AIDS. People can die from overdose: they stop breathing. Tolerance happens over time; that is, more and more of the drug is needed to get the same effect until at last there is no effect—the user takes it just to keep from getting sick. Most users are in poor health, mostly because they do not take care of themselves properly, and take physical risks.

CLASSIFICATION

Depressant. Narcotics slow everything down and can cause people to fall asleep, or stop breathing.

MEDICAL USES

Pain relief

LEGAL OFFENSES

Having it, selling it, or having enough of it that the court thinks that you intended to sell it, sending it, lending it, offering to sell it.

SLANG NAMES

Heroin:

- "Smack"
- "Junk"
- "H"
- "Horse"

Others:

- "M"
- "Percs"

SYMPTOMS and BEHAVIORS

Users "coast"—as in a dreamy half-awake state (usually followed by feeling very down). Users cannot control hands or legs or speech; appetite usually goes and often accidents occur. Urge for the drug is so strong that to get it, users may attack people they love, or steal. When addicts cannot get the drug, they vomit get watery eyes, runny nose, hot and cold flashes, muscular cramps, and diarrhea.

NICOTINE

EXAMPLES

Cigarettes
Cigars
Pipe Tobacco
Chewing Tobacco
Snuff
Smokeless Tobacco

MAJOR DANGERS

Users get addicted to it. Those who keep using it can get cancer of the lung, mouth, throat, or stomach; bronchitis and emphysema (a lung disease that takes a long time to kill), and eye problems. Nicotine is a major cause of heart attacks. Many die prematurely from the effects of smoking.

CLASSIFICATION

Nicotine speeds up the body's workings and slows them down.

MEDICAL USES

None

LEGAL OFFENSES

Under federal law, it is illegal to sell to persons under 18 years of age. There are many places where smoking is forbidden.

SLANG NAMES

"Coffin Nails"
"Cancer Sticks"
"Smokes"

SYMPTOMS and BEHAVIORS

Blood pressure goes up, heart rate is too fast, and if smokers use enough, they can get the shakes, have trouble breathing, and may develop kidney damage. Users usually emit an unpleasant odor.

ORGANIC SOLVENTS

EXAMPLES

Model Airplane Glue
Nail Polish Remover
Dry Cleaner Fluid
Gasoline
Paint Thinner
Lighter Fluid
Plastic Cement

MAJOR DANGERS

Chronic use causes damage to the brain, liver, and/or kidneys. Sniffing solvents can cause sudden death due to heart failure. The user may commit crimes, get into fights, and have accidents. Sometimes users die accidentally from choking or from suffocation. Other dangers are similar to those of cannabis or LSD, with the added risk of sudden death.

CLASSIFICATION

Depressants. These solvents slow everything down and can cause people to fall asleep, or to stop breathing.

MEDICAL USES

None

LEGAL OFFENSES

Not covered by law

SLANG NAMES

None

SYMPTOMS and BEHAVIORS

Users behave as if drunk and sometimes smell of solvents. Users get confused, cannot talk coherently and sometimes become very suspicious and/or violent. They may see and hear things that aren't there. They cannot control what their muscles do and often have a runny nose and watery eyes. Users may be grouchy, sleepy or become unconscious.

SEDATIVES AND HYPNOTICS

EXAMPLES

Sleeping Pills
Other Barbiturates

MAJOR DANGERS

Severe addiction can happen. Users cannot think coherently and lose muscle control. There can be damage to the liver and the brain. Users die from overdose either by the drug alone or by mixing it with some other drug, such as alcohol. It is dangerous to quit without a doctor's advice and supervision, partly because serious, sudden convulsions or seizures may occur.

CLASSIFICATION

Depressants. These substances slow everything down and can cause users to fall asleep, or to stop breathing.

MEDICAL USES

To treat insomnia, anxiety, nervous tension and epilepsy; they are also used in the treatment of mental disorders.

LEGAL OFFENSES

Selling it, or having enough of it that the court thinks that you intended to sell it, are crimes. It is also a crime to make or process any of these drugs.

SLANG NAMES

"Goofballs"
"Red Devils"
"Seckies"
"Tooies"
"Nemmies"
"Rainbows"
"Christmas Trees"
"Downers"
"Downs"
"Reds"

SYMPTOMS and BEHAVIORS

Users behave very much as if they were drunk. They usually have little energy and feel down much of the time. Pupils of the eyes may shrink to the size of pinpoints.

STIMULANTS (1)

EXAMPLES

Amphetamines (Speed or Uppers)
Benzedrine
Dexedrine
Methedrine
PMA
TMA
Phentermine

MAJOR DANGERS

Users of these drugs do not eat properly, cannot sleep properly, and often develop paranoia (they believe others are out "to get" them). They can get pneumonia, severe high blood pressure, or heart attacks and/or brain damage (for instance by a stroke). Sudden death may occur. These drugs reduce the appetite. Addiction happens fast and is very strong. Users take many foolish chances and often become violent because they cannot trust anyone. There is a tolerance effect, which means users must take more to get the same effect.

CLASSIFICATION

Stimulants. They speed up the body's workings.

MEDICAL USES

To relieve mild depression and fatigue. To treat narcolepsy (a rare disease in which there is an uncontrolled desire to sleep). To treat hyperkinesis (overactive condition) in children.

LEGAL OFFENSES

Selling it, or having enough of it that the court thinks that you intended to sell it, are crimes. It is also a crime to make or process any of these drugs.

SLANG NAMES

For Pills and Capsules:

"Uppers"
"Ups"
"Pep Pills"
"Bennies"
"Beans"
"Dexies"
"Hearts"
"Peaches"

For Methamphetamines (usually injected):

"Speed"
"Crystal"
"Meth"

SYMPTOMS and BEHAVIORS

Pupils of the eyes get big. Users lose appetite, are talkative, grouchy and jumpy. Users get a bad complexion; the nose and mouth dry out. Users are either tired or overactive. If users take enough, they can believe things that aren't true, get violent and can behave in many of the way described for LSD.

STIMULANTS (2)

EXAMPLES

Cocaine
Coca Leaves

MAJOR DANGERS

Cocaine is a very powerful stimulant and does all the things listed above for amphetamines, and is even more addictive. Sudden death may occur. Users get addicted to it and will use as much as can be found. Users will be confused, have memory problems, cannot think straight and often have dizzy spells.

CLASSIFICATION

Stimulant. It speeds up the body's workings.

MEDICAL USES

Local anesthetic (rare).

LEGAL OFFENSES

Having it, selling it, having enough of it that the court thinks that you intended to sell it, sending it, lending it, offering to sell it.

SLANG NAMES

"Snow"
"Coke"
"Nose Candy"

SYMPTOMS and BEHAVIORS

Much of the same as for speed and other uppers. While on the cocaine high, users wrongly think they can do anything, can make no mistakes. But judgment goes when on a high, and the high is so attractive users will go broke buying it. Often users steal and deal to pay for the habit.

STIMULANTS (3)

EXAMPLES

Crack (Crack is cocaine in a much stronger and smokable form)

MAJOR DANGERS

It does all that cocaine does, only faster and with more severe results.

CLASSIFICATION

Stimulant. It speeds up the body's workings.

MEDICAL USES

None

LEGAL OFFENSES

The same as cocaine.

SLANG NAMES

"Crack"
"Rock"

SYMPTOMS and BEHAVIORS

Crack brings addiction as fast as any drug, and much faster than most. Not only do users want the high again, but the down that follows is so bad it cannot be tolerated. The high and the down are barely 10 min apart, so crack users usually cannot think of anything but wanting the high again. Stealing is more unplanned than the cocaine user's—crack often leads to purse snatching and mugging.

TRANQUILIZERS

EXAMPLES

Miltown
Equanil
Valium
Librium
Serax
Ativan
Halcion

MAJOR DANGERS

Besides the real danger of strong addiction, users of these drugs may get to a point where there are memory problems and users just aren't as alert as they normally would be. These drugs cause driving impairment. As with any other depressant, tranquilizers become especially dangerous when mixed with any other drugs, often death by overdose happens because users mixed the tranquilizer with alcohol, sleeping pills or pain killers. As with the sedatives/hypnotics it is dangerous to get off tranquilizers without a doctor's advice and supervision.

CLASSIFICATION

Depressant. Tranquilizers can slow everything down and can cause people to fall asleep or to stop breathing.

MEDICAL USES

Psychiatrists and other doctors may prescribe tranquilizers to reduce severe anxiety or nervousness, often to enable a very anxious person to talk to a counselor. Doctors may also prescribe them for certain kinds of muscle problems.

LEGAL OFFENSES

Selling it, or having enough of it that the court thinks you intended to sell it, are crimes under the Food and Drugs Act. It is also a crime to make or process any of these drugs.

SLANG NAMES

"Downs"
"Tranks"

SYMPTOMS and BEHAVIORS

Tranquilizers work much like the sedatives and hypnotics listed above. Users may not see very well and may seem forgetful and confused; there can be dizziness or drowsiness. Sometimes users' speech is slurred and they may get a skin rash or have unexplained sweating.

Pattern Recognition

Drugs are not good or bad in themselves. They may be used properly or abused. Similarities in structural formulas of drugs cause similar physiological responses.

Common Student Misconceptions

1. **"Bufferin is twice as fast as aspirin. Bufferin helps prevent the stomach upset often caused by aspirin."** The FDA investigated these advertising claims and did not find the claims to be true.
2. **"Chicken soup is the best cure for the common cold."** There is no scientific evidence that chicken soup can cure the common cold. Plenty of liquids and rest, and 5-7 days of suffering are the best cures.
3. **"One of my friends took a drug once and got better."** This statement is nonspecific and says nothing about drug effectiveness.
4. **"There is only one kind of alcohol."** The "one kind of alcohol" typically thought of is ethanol or ethyl alcohol. Methyl alcohol and isopropyl alcohol are other alcohols.
5. **"More is better."** This typically refers to minerals and vitamins that are needed by the body in small amounts. Taking megadoses of these substances can cause some unexpected problems. For example, too much vitamin D can cause pain in bones, nausea and diarrhea, and weight loss. Too much salt (NaCl) in the diet can cause elevated blood pressure in some individuals.
6. **"Walking across a field of poppies will put you to sleep."** (From the Wizard of Oz.) When Dorothy and her friends in the Land of Oz walked across the poppy fields, they fell asleep. Although opium poppies contain morphine, a central nervous system depressant, walking through a poppy field will not cause one to fall asleep. The morphine must be extracted; *in situ* it is nonvolatile.
7. **"Antiseptic, antibiotic, analgesic, and anti-inflammatory mean the same thing."** These terms do not mean the same thing and the distinction among them was described in this module.
8. **"Two extra strength aspirin are better than 3 regular aspirin."** Three regular aspirin contain 975 mg (3 x 325 mg) of active ingredient. Two extra strength aspirin contain 1000 mg (2 x 500 mg) of active ingredient. The difference (25 mg) is not enough to make a significant difference.
9. **"Receiving a vaccine guarantees immunity."** A vaccine is designed to cause a person to build a resistance to a viral infection (*e.g.*, mumps, polio). When given a vaccine, some individuals have developed serious cases of the disease that the vaccine is designed to alleviate.

Classroom Discussion

Classroom discussion is particularly important in this module. Suggested points for discussion are indicated below.

1. Why do people smoke or use drugs if we know that they are bad for you? (The discussion will avoid judgmental aspects and will address the social problem.)
2. How is the legal use of alcohol and cigarettes different from the illegal use of pleasure drugs?
3. To what extent is the use of anesthetics warranted in ordinary cuts and bruises, dentistry, and childbirth?
4. At what point in an illness should the decision to use or terminate chemotherapy occur?

HISTORY: ON THE HUMAN SIDE

For centuries, humans have eaten or chewed berries, bark, roots, and herbs to alleviate or cure sickness or disease. The origin of disease was unknown, and its treatment was coupled with magic and superstition. However, the scientific practice of medicine began in ancient Asiatic civilizations. The first known code of medical ethics was established in Sumer. The ancient practice of acupuncture and ideas about blood circulation suggest that the Chinese were familiar with anatomy, vascular systems, and the nervous system. In addition to introducing the Hippocratic oath, the Greeks advanced medical knowledge in anatomy and physiology, diet, and exercise. Through their sanitation facilities, the Romans improved public health. Medical knowledge began to decline during the Middle Ages in Europe, but Arab and Jewish physicians made some progress. For example, two Persians introduced opium for coughs and extracts of crocus seeds to treat gout. Both of these remedies are in use today.

The ancients knew that chewing willow tree (Genus: *Salix*) bark had an analgesic effect. Centuries later, the active ingredient was isolated from the willow bark and called salicylic acid in deference to its origin.

Jesuit missionaries introduced an important herbal remedy into Europe in the 17th century. This remedy was an extract of cinchona bark obtained from South American Indians. The extract was used by Indians against chills and fever and soon became a favorite anti-malarial medicine in Europe. The principal ingredient of cinchona bark is quinine. Also, in the 17th century, William Harvey demonstrated blood circulation and the heart as a pump. A major step toward diagnosing disease was made with the introduction of the compound microscope, making minute forms of life visible for the first time. The 18th century witnessed the introduction of vaccination by Edward Jenner.

Modern medicine had its birth in the 19th century with the development of the germ theory of disease, the use of anesthesia (Crawford Long, 1842), antiseptics in surgery (Joseph Lister, 1867), and a revival of public health measures and better sanitation. During the 20th century there has been an increased understanding of immunity, the endocrine system, and the importance of vitamins and nutrition, advances in surgery, organ transplants, and diagnostic techniques (CAT scan, MRI, *etc.*). Chemotherapy is an important development of the 20th century. Specific drugs have been discovered and designed to eliminate disease-causing microorganisms (antibiotics), to rectify a hormonal imbalance (insulin), and to arrest a cancerous growth (anticancer drugs).

The following are three interesting stories related to chemistry in medicine. The first two are taken from *Men of Medicine* by Katherine Shippen (1957). The last is from *Medical Heroes and Heretics* by Wayne Martin (1977).

Who Discovered Anesthesia?

In the eighteenth century, the English chemist Humphry Davy made dinitrogen oxide (N_2O, nitrous oxide, laughing gas), and observed that it prevented feeling physical pain. He thought it might be useful in surgery, but did nothing about it. It wasn't until the next century that a true anesthetic was made, although its discoverer has not yet been satisfactorily determined.

As towns sprang up in the West and South of the United States, people were entertained by showmen who featured laughing gas in their repertoire. At one of these laughing gas shows in December 1841, the Georgia physician Crawford Long observed its effects first-hand. Long was very popular with young people, and when his young friends asked him to prepare them some laughing gas, he told them he lacked the apparatus for making it but that he had a medicine called sulfuric ether that would do as well. He sometimes gave a few drops of this compound to nervous patients. Some of his friends tried inhaling sulfuric ether, others soon followed suit, and before long ether parties were being held all through the county. People affected by the gas would throw themselves about hilariously, knocking against furniture, often falling down, bruising themselves, and scraping shins and elbows. Although the cuts and bruises were often considerable, the participants at the ether frolics never complained of them. They didn't even seem to notice that they had hurt themselves. Long correctly reasoned that the ether prevented their feeling pain.

Long decided to use the ether in an operation to remove two small tumors on the back of the neck of a young patient. He let the patient inhale some ether and, after the muscles completely relaxed, removed the tumor. Long recorded the surgery in his ledger, but did not report this first surgery under ether (1842) to a medical journal. Whatever the reason, it was a shock to him to read in a medical journal four years later that William Morton in Boston had administered a gas to a patient that made him insensible to pain.

Morton received much acclaim for his discovery and Long grew bitter over his neglect in reporting his own discovery. When he served in the Civil War, Long kept his ledger with the entry of his discovery with him. Upon his return home after the war, he placed the ledger in a trunk in the attic. His family never dared to speak of the discovery since the mention of it distressed Long too much.

Meanwhile, Morton received permission to demonstrate his ether in surgical operations before the great surgeons at Massachusetts General Hospital. The doctors were interested in seeing the preparation that diminished the sensibility to pain. Morton administered the drug to a patient who shuddered a little and then fell into a deep sleep. Morton removed a large tumor of the jaw, and the patient did not stir as the knife cut into his flesh. After regaining consciousness, the patient said the surgery hadn't hurt at all. Oliver Wendell Holmes, the poet and physician, suggested the word "anesthesia" to Morton in late 1846. According to Holmes, the term signified insensibility to touch.

Discovery of Penicillin

In 1914, Alexander Fleming, physician in the Royal Army Medical Corps, observed that many soldiers wounded in combat developed blood poisoning, pneumonia, or some other bacterial infection. Fleming knew there was need for an effective antiseptic to fight the infections, but none was available.

After the war, Fleming began to teach bacteriology at St. Mary's Hospital in London. He spent many hours in the laboratory searching for the microbe-destroying agent he had needed during the war. One day in 1928, he observed through his microscope that a mold fleck had settled on one culture plate of bacterial growth sitting next to an open window. At first he was annoyed that the mold had contaminated the plate. About to throw it away, he stopped and examined the plate again. The mold was being surrounded by a halo of watery fluid, and he surmised that something in the mold was destroying the microbes. He removed the mold and grew more of it. At first it was fuzzy white, then it turned green, spreading fronds that matted together in a thick mass. Fleming and his assistants continued to study the watery fluid secreted by the mold and found that it was effective against germs causing blood poisoning, sore throat, some types of pneumonia, but not typhoid fever or dysentery. It did not affect blood serum as he had feared it might, nor did it harm mice and rabbits. He concluded that it could be applied to the infected surface undiluted, and it was nonirritating and nontoxic. He named the new antiseptic penicillin, after the *penicillium* family to which the mold belonged.

In 1929, Fleming published a paper announcing the discovery of penicillin. The tiny amounts of penicillin that Fleming could make in the laboratory were not enough to treat a single patient, so his discovery did not arouse much interest. His paper lay forgotten on the library shelves for nearly 10 years until, in 1939, an Australian physician, Howard Florey, reread it and contacted Fleming. Fleming sent Florey some of the original mold, and from it Florey eventually isolated about a teaspoonful of penicillin—enough to treat one case of infection. He soon had the opportunity to find out if it worked: as a last resort he administered the penicillin to a policeman with a severe case of blood poisoning. The penicillin combated the blood poisoning effectively as long as it continued to be administered, but the single teaspoonful was not enough. When the penicillin ran out, the blood poisoning returned, and the patient died. Florey knew that larger amounts of penicillin would have to be made on a commercial scale. Because England was involved in a war in 1941, Florey went to the United States where penicillin could be mass-produced. By 1943, it was being used to treat infected wounds of the armed forces. Since that time, many lives have been saved by this so-called "miracle drug." Fleming and Florey shared the Nobel Prize for medicine in 1945 for their discovery.

Jonas Salk and the Polio Vaccine

In 1921, while vacationing on the Island of Campobello off the coast of Maine in New Brunswick (Canada), Franklin D. Roosevelt was stricken by paralytic polio and was crippled for life. In 1926, he established the nonprofit Warm Springs (Georgia) Foundation for treating polio victims. The March of Dimes program, which was associated with the foundation, amassed over $500 million to help polio victims, designating some $40 million to finance polio research. In this research endeavor, the conflict of heresy and established belief developed, yet both produced results. The heretic was Jonas Salk. His heresy was the use of a killed-virus vaccine.

In 1908, Karl Landsteiner (Austria) established that polio was caused by virus. By 1941, there were three general types of polio virus had been identified; it had also been determined that all strains of one type would immunize against strains of that type only. By 1952, it was known that polio virus circulated in the blood, and this fact proved to be its Achilles heel since a vaccine-produced antibody in the blood could protect against polio. Isabel Mountain prepared a killed vaccine using formaldehyde to inactivate the virus. She discovered that the killed-virus vaccine would produce a degree of immunity in a monkey without harm.

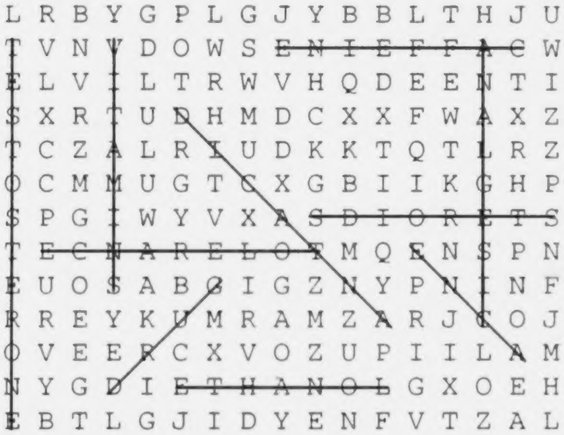
Given these bits and pieces, what was Jonas Salk's claim to fame? Salk put all the pieces needed for eradication of the disease together by acting quickly and with great precision. In 1947, Salk, then 33, was Research Professor of Bacteriology and Pathology at the University of Pittsburgh. He undertook a program of typing the approximately one hundred strains of polio virus that had been isolated. He became bored during the latter part of the three-year program and began to look ahead to develop a vaccine based on the knowledge available to him. The typing program confirmed that their were only three types of polio virus. In 1951, Salk made a killed-virus vaccine—by treating polio viruses with formaldehyde at 36 °C for 11–13 days. This killed-virus vaccine produced a high degree of immunity to all three types of polio in monkeys contrary to the belief at the time that a killed-virus vaccine could not mobilize antibodies. Salk continued to run tests to ensure that his vaccine was safe by repeatedly determining that the vaccine contained no live virus. He tested his vaccine in immune children (who had had a previous paralytic infection of polio). In all cases some increase in antibody production was noted. In 1953, confident of his vaccine, Salk tested himself, his family and about 400 volunteers in Pittsburgh. One year later the vaccinated subjects were retested and found to have the same high level of vaccine-induced antibodies. Children were vaccinated before the polio seasons of 1954 and 1955. The test showed the vaccine to be safe and effective.

The medical establishment, led by Albert Sabin, complained about the use of the killed-virus vaccine. Sabin claimed that if live virus remained in the vaccine and it were used, it would kill and cripple. Sabin and his colleagues felt that use of a weakened live-virus vaccine was preferable. Throughout his preparation of the killed-virus vaccine, Salk made every effort to ensure that no live virus was present. Yet unintentionally, Salk hurt many feelings and stepped on many tender toes in the process. The ill will of the scientific community hurt Salk deeply, and he retreated into the seclusion of his laboratory at a time when the public wanted to give him a tickertape parade.

In 1955, a commercial laboratory carelessly produced and sold batches of Salk vaccine containing unkilled viruses. The defective vaccine caused 204 polio cases with 11 deaths and over 100 cases of paralysis. Albert Sabin and the establishment rallied with an attack of vigor and by 1956, the medical establishment had produced a weakened, live virus vaccine (the Sabin vaccine). In 1964, the Surgeon General stated there was only a small risk involved with the Sabin vaccine. He failed to mention that with the killed Salk vaccine, properly prepared, there was no risk at all. The Salk vaccine became passé. Today, the Sabin vaccine is preferred by physicians.

HUMOR: ON THE FUN SIDE

1. Word Search (see *Appendix* for master copy)



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L R B Y G P L G J Y B B L T H J U
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Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Substance that reacts with excess stomach acid.
2. Common name for a substance that changes a physical or psychological function in the body.
3. Need of increasing amounts of a substance to experience the same initial effects.
4. Acetaminophen, ibuprofen, or acetylsalicylic acid, for example.
5. Benzoyl peroxide is the active antiseptic ingredient in ____ ointments.
6. These organic compounds are required in small amounts in the diet.
7. Stimulant in cola and coffee.
8. Birth control drugs belong to this class of organic compounds.
9. The amount of this drug is determined in the Breathalyzer test.
10. Anabolic steroids are synthetic derivatives of this natural compound.

Answers: 1. ANTACID 2. DRUG 3. TOLERANCE 4. ANALGESIC 5. ACNE 6. VITAMINS 7. CAFFEINE 8. STEROIDS 9. ETHANOL 10. TESTOSTERONE

2. See cartoons at end of module.

MEDIA

1. The CHEM Study film "Molecular Structure and Health." Time-lapse photomicrography of laboratory demonstrations helps to identify the role of molecular structure in determining biological activity. Students will also see how the correlation of the structure and biological activity of sulfanilamide with a vitamin essential for bacterial growth leads to a more general presentation of the biochemical nature of growth. Color, 22 min. Available from Ward's Natural Science Establishment, Inc., 5100 West Henrietta Road, P.O. Box 92912, Rochester, NY 14692-9012, (716) 359-2509, (800) 962-2660; (716) 334-6174 FAX.
2. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).
    a. For the Apple II computer running on ProDOS: AR 702
    b. For the Apple II computer: AP 701
3. Videodisc published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

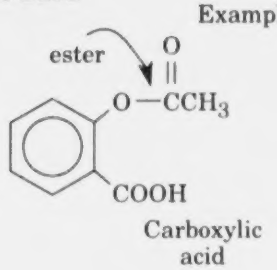
"From an Amino Acid to a Peptide Chain," "The Alpha Helix," and "DNA Structure, Synthesis of Messenger RNA, Protein Synthesis," three chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc II (double sided, 60 min.), Special Issue 4.

Links/Connections

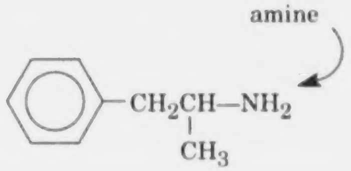
WITHIN CHEMISTRY

1. **Organic Functional Groups**. Structurally, many drugs are carboxylic acids, alcohols, amines, esters, ethers, aldehydes, and/or ketones.

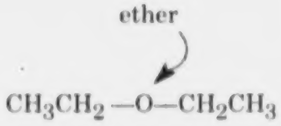
Examples are:



Aspirin
analgesic



Amphetamine
stimulant

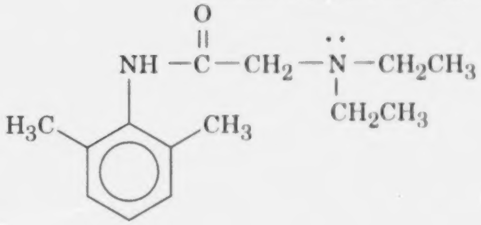


$CH_3CH_2-O-CH_2CH_3$

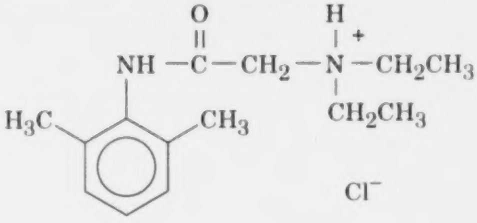
Diethylether
anesthetic

2. **Nomenclature**. Several names can be used to specify a drug. Generic names are often used. The brand name (or trademark name) is the name adopted for use by the drug company that markets the drug. Each company chooses its own trade name. There is only one generic name for each drug, but there may be many brand names. For example, acetaminophen (generic name) is sold as Tylenol, Tempra, Datril, Liquiprin, and Trilium (brand names). Drugs are also referred to by street names (see Drug Reference Chart in *Tips for the Teacher* section).

3. **Acids and Bases**. Pain sensation arises from a response of nerve endings to a change in pH of solutions around them. Neutralization of the solution in the tissues that is causing the irritation or pain relieves the pain. Certain organic functional groups are responsible for the acidic or basic properties of these substances. For example, lidocaine, a local anesthetic used by dentists, contains a basic amino group. To minimize the local irritation and discomfort when lidocaine is used, it is administered as a neutral salt solution.



Lidocaine
(xylocaine)
with basic amino group



Lidocaine Hydrochloride
(xylocaine)
neutral

4. **Extraction**. Many of the active ingredients in plants contain basic nitrogen atoms and can be extracted from the bulk of the plant material by dilute acid. Because these compounds behave similar to an alkali, they are referred to as alkaloids.

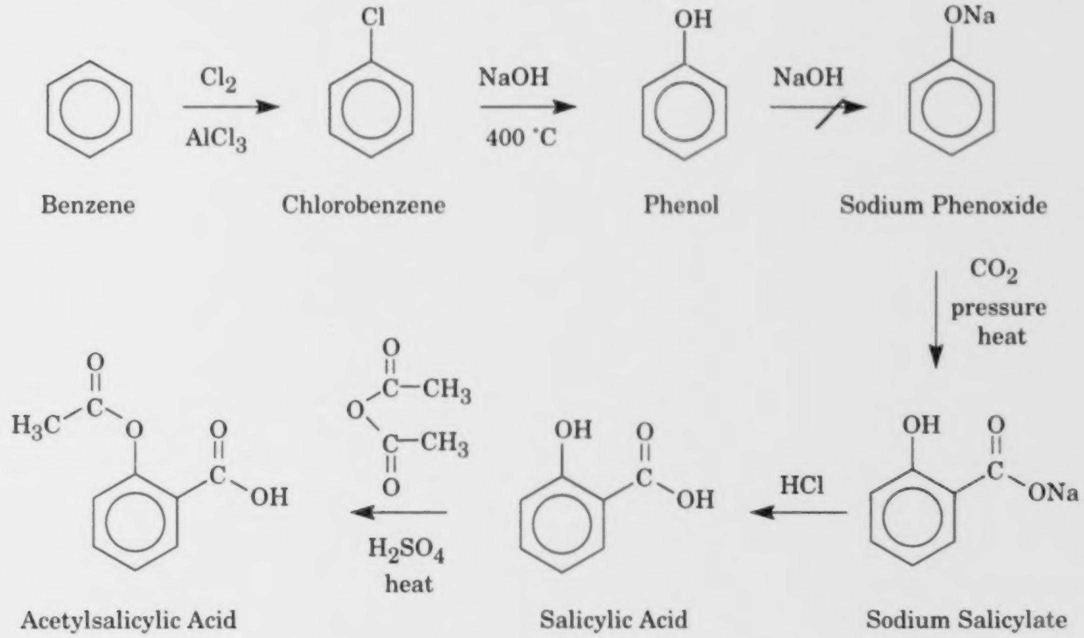
$$R_3N: + H^+(aq) + Cl^-(aq) \rightarrow R_3NH^+Cl^-(aq)$$

After extraction, free alkaloids can be regenerated by treatment with aqueous base.

$$R_3NH^+Cl^- + OH^- \rightarrow H_2O + Cl^- + R_3N\!:$$

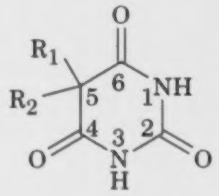
Cocaine, morphine, and atropine are obtained in this way.

5. **Synthesis**. Drugs that do not occur naturally in plants or animals must be synthesized in the laboratory. Many naturally occurring drugs are also synthesized to increase cost effectiveness and supply. Although salicylic acid is a good analgesic and antipyretic, it is sour and irritating when taken orally. Chemists modify the molecule's structure to remove this undesirable property while retaining the desirable medicinal property. Acetylsalicylic acid (aspirin) is prepared from salicylic acid by treatment with acetic anhydride (see *Activity 1*). Salicylic acid is made from benzene, which is obtained from coal tar.

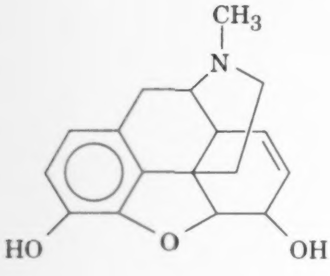


6. **Structure-Activity Relationships**. Chemists have determined the structures of many naturally occurring biologically active compounds. Such information is useful in relating pharmacological action to chemical structure within a group of compounds with similar action.

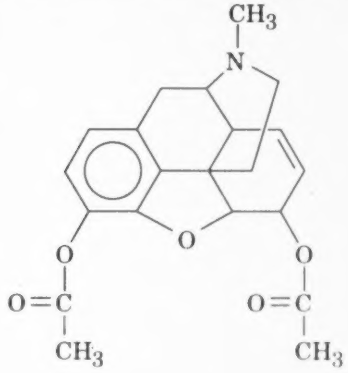
Barbiturates contain the ring structure shown. Variation of the R groups at C-5 can modify the sedative-hypnotic action. For example, incorporating a phenyl group (C_6H_5–) yields a barbiturate that is less water soluble and more resistant to biodegradation and is therefore longer acting. Researchers can synthesize many different barbiturates and select those with the greatest promise.



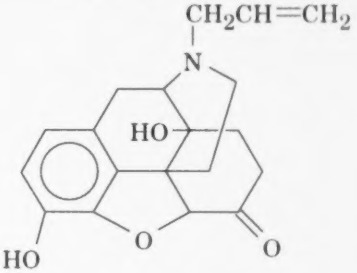
The analgesic properties of morphine are due to the presence of hydroxy, ether, and amine groups that help bind it to the receptor site. Heroin is easily converted in the human body to morphine in an enzyme-catalyzed hydrolysis of the two ester (CH_3COO-) groups. Naloxone is a narcotic antagonist. By changing a hydroxy group to a ketone ($-C{=}O$), a methyl group to an allyl group ($-CH_2CH{=}CH_2$), introducing another hydroxy group, and by reducing a double bond, the drug still fits the opiate receptor sites in the brain but has lost all of its narcotic and respiratory depressant activity.



Morphine

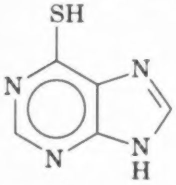


Heroin

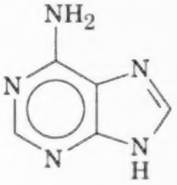


Naloxone

In another example, cancer has been successfully treated using the structure-activity relationship. Mercaptopurine is similar to the real metabolite adenine. Rapidly growing cancer cells can mistake mercaptopurine for adenine. Mercaptopurine is an analog of hypoxanthine from which adenine is synthesized. When this molecule is incorporated as a "useful" metabolite into cancer cells, cell growth is impeded. Mercaptopurine is called an **antimetabolite**. Although effective in cancer treatment, antimetabolites also harm normal cells.



Mercaptopurine



Adenine

7. **Stereochemistry**. Benzedrine's active ingredient is the dextrorotatory form in a racemic mixture. Cisplatin is only an active chemotherapeutic in the *cis*-form. Transplatin has no therapeutic effect. These steric effects are a special case of structure-activity relationships.

8. **Instrumentation and diagnosis**. *Magnetic resonance imaging* (MRI) is a technology based on the same principle of operation as a nuclear magnetic resonance spectrometer used by chemists in structure determination (see *Instrumentation* module). The MRI scans the individual without exposing the patient to X-rays (as in CT scan) or gamma radiation (as in PET scan). In MRI, a low energy radiofrequency wave interacts with the hydrogen atoms in water molecules in soft tissue. The energy produced from this interaction is fed into computers that produce an image similar to that of CT and PET scans. MRI has proved to be useful for studying soft tissue (tumors, cancerous tissue, the pelvic area, prostate gland, and bladder). Use of this technique has improved the diagnosis of cancer in these soft tissues.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

1. **Botany**. Plants are an important source of drugs. Many of these drugs are legal, but some are drugs of abuse. Plants were used by early humans in religious rituals (peyote), medically (to treat diarrhea or worm infestation), and as poisons (Socrates' cup of hemlock tea that contained the active ingredient coniine). Examples of plant-source drugs in use today are shown here.

Drug	Plant source
Mescaline	Peyote cactus
Caffeine	Coffee arabica
Caffeine	Camellia thea
Cocaine	Erythroxylon coca
Marijuana	Cannabis sativa
Nicotine	Nicotiana rustica

2. **Pharmacology**. When a drug is administered orally, it follows the pathway shown here:

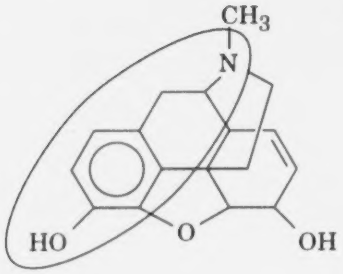
$$\begin{tikzcd}
\text{stomach} \arrow[r] & \text{intestine} \arrow[r] \arrow[d] & \text{blood} \arrow[r] \arrow[d] & \text{target} \\
 & \text{excretion} & \text{excretion} &
\end{tikzcd}$$

When a drug is administered by injection into fat or muscle tissue, the intestinal tract is not involved, and the drug finds its way into the blood stream and then to its target. The mechanisms by which some drugs function are summarized below:

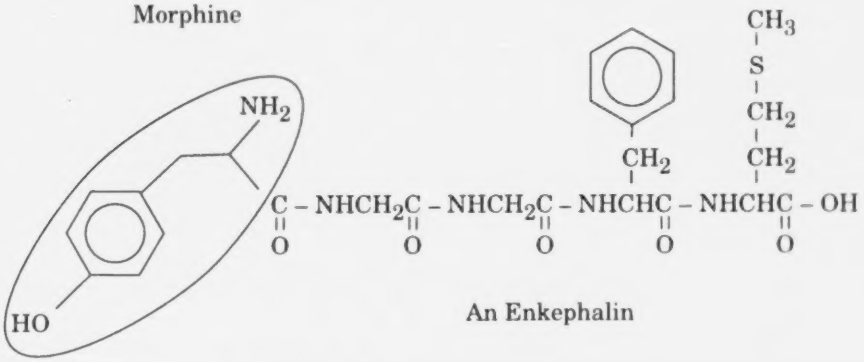
a. **Analgesics and antipyretics**. These drugs inhibit the synthesis of prostaglandins that are responsible for perception and a rise in body temperature.

b. **Local anesthetics**. These drugs block nerve impulses to the brain.

c. **Morphine, codeine, and meperidine**. Receptor sites in the brain accept naturally produced substances released as a response to pain (enkephalins). Morphine, codeine, and meperidine have structures that are similar to the enkephalins and can fit the brain's receptor sites. The better the fit, the better the analgesic action. Note the structural similarity (circled areas) in each structure, as shown.

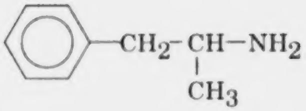


Morphine

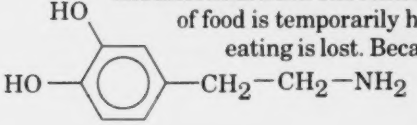


An Enkephalin

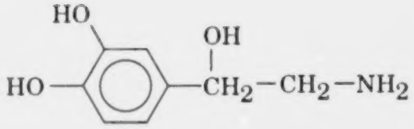
d. **Amphetamines in weight control**. An excited or angry person secretes extra dopamine and norepinephrine. These are then distributed to the brain and intestinal tract. The central nervous system is stimulated, and digestion of food is temporarily halted to the extent that interest in food and eating is lost. Because amphetamines are structurally similar to these two body chemicals, they produce the same kind of intestinal tract suppression.



Amphetamine
(Benzedrine)



Dopamine



Norepinephrine

e. **Alcohol**. A liver enzyme causes the oxidation of ethanol to acetaldehyde (CH_3CHO), then to acetic acid (CH_3COOH), and finally, to CO_2. The "belch" associated with drinking beer is due to the buildup and release of carbon dioxide in the beer (see *Links and Connections within Chemistry* in the *Organic Chemistry* module for additional discussion of alcohol metabolism).

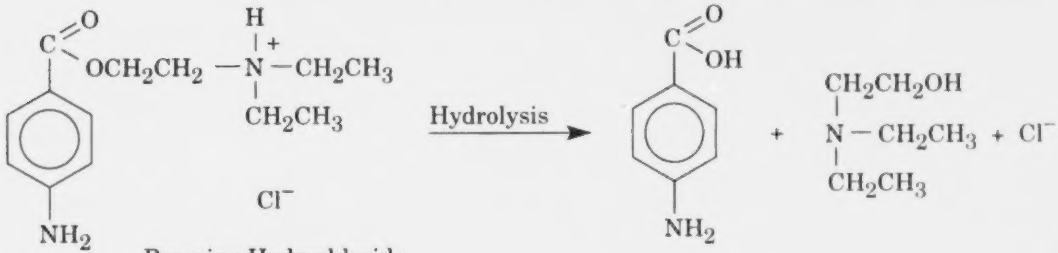
f. **Alkylating agents**. These agents transfer alkyl groups to guanine, a nitrogen base in DNA, blocking base pairing and preventing DNA replication. Healthy cells are harmed as well. (Alkylating agents are used in the treatment of cancer.)

g. **Antimetabolites**. These agents interfere with DNA synthesis by inhibiting the formation of thymine-containing nucleotides. (Antimetabolites are used in the treatment of cancer.)

h. **Penicillins**. Penicillins prevent cross-linking in the formation of bacterial cell walls. Human cells are of a different chemical composition and are not affected.

i. **Birth control pills**. The synthetic progesterone blocks the release of a hormone that stimulates the ovaries to release an egg. If an egg isn't released, pregnancy is impossible.

3. **Biochemistry**. Nearly all the drugs we take are foreign to the body. The process by which the body accepts a drug, alters it chemically to eliminate the drug action, and then prepares it for excretion is called metabolism. The product of chemical breakdown of a drug is called a metabolite. Drug metabolism occurs primarily in the liver. The liver changes a drug chemically so that the metabolite is more soluble in the aqueous medium of the urine. Chemically, these processes involve hydrolysis, attachment to a normal body substance, oxidation, or salt formation. For example, the local anesthetic procaine (Novocain) is hydrolyzed to *p*-aminobenzoic acid, which has no anesthetic effect but, more importantly, is more water soluble than procaine.



Procaine Hydrochloride
(Novocain)

p-aminobenzoic acid

4. **Genetics**. In any population, there are individuals who are sensitive to a given drug and those who are resistant. The resistance is imparted by the genetic composition of the individual. Resistance to antibiotics by certain microorganisms is an example of this phenomenon. Broad spectrum antibiotics have been developed to encompass a greater number of the resistant population.

TO THE CONTEMPORARY WORLD

Community

Knowledgeable individuals: pharmacists, nurses, physicians, hospital directors, drug unit in a police department

Societal (Science/Technology/Society; current events)

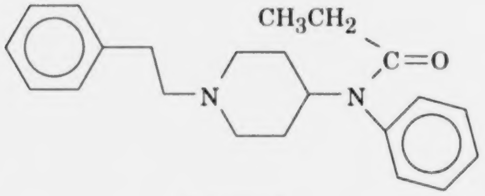
1. **Drug dependence**. Dependence is a situation in which drug users develop reliance, either physical or psychological. Tolerance and withdrawal are not necessarily seen. For example, cocaine induces a psychological dependence, but does not induce the development of tolerance. (Addiction is a drug-induced change in the physical state of an individual characterized by a development of tolerance and withdrawal syndrome).

2. **Drug testing in Olympic games**. Drug testing is an integral part of the Olympic Games. The International Olympic Committee uses instrumentation (primarily gas chromatography and mass spectroscopy) to detect drug use prior to an athlete's competition. The first four finishers plus one random competitor provide a urine sample within 1 hr of the competition's end. Drugs that have been banned include amphetamines, narcotics, analgesics, anabolic steroids, diuretics, and beta blockers. Athletes must be careful not to use cold medicines that contain ephedrine, pseudoephedrine, or phenylpropanolamine as these drugs could give false positive tests for amphetamines. Some anabolic steroids can be detected months after the last use; termination just before a competition will not normally avoid detection.

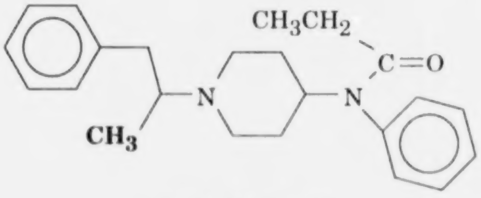
3. **Drug testing in the workplace**. Reduced productivity due to alcohol and drug abuse costs the federal government and society in general billions of dollars each year. Drug use on the job can result in accidents, absenteeism, health problems, memory loss, turnovers, and loss of skills and coordination. Such problems have caused segments of government and private industry to institute drug testing. Alcohol and marijuana are drugs commonly abused, but amphetamines, barbiturates, cocaine, and opiates are also abused. If an individual is a government employee, the employer must have probable cause before the individual can be tested. Private employers have the right to demand drug tests at hiring time.

4. **Drug equivalence**. Unless the physician has prohibited substitution of a generic drug for a brand name drug, pharmacists may substitute a less expensive generic drug. In many cases, generic name drugs cost one-fourth as much as their brand name equivalents. The concern for the consumer is the equivalency in effectiveness of the generic drug. Studies have shown that differences in absorption of brand name and generic drugs into the bloodstream are very small.

5. **Drug design versus designer drugs**. Designer drugs are substances contrived in illegal laboratories to be chemical analogs of well-known controlled substances. Their slight difference in chemical structure renders them outside the jurisdiction of the law. Shown here is the structural relationship between the narcotic analgesic Fentanyl and its analog, α-methyl fentanyl.



Fentanyl

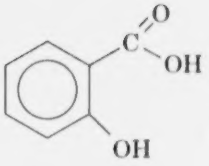


α-methylfentanyl

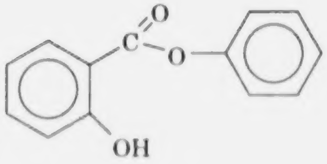
The minor structural change does not alter the fundamental analgesic nature, but α-methylfentanyl is a more powerful narcotic than Fentanyl. Many of today's designer drugs were synthesized years ago by legitimate medical researchers but rejected because of serious adverse effects.

Drug design, on the other hand, is the synthesis and study of legal substances to treat a particular disease or condition. Chemists have designed molecules to relieve headaches, cure infectious diseases, prevent conception, and kill cancer cells (see examples in *Tips for the Teacher* section).

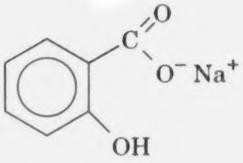
Salicylic acid, extracted from willow bark, was found to be useful in reducing fever and pain. However, it is sour and irritating when taken orally. Chemists sought to modify the structure of the molecule to remove this undesirable property while retaining and improving the desirable properties. The first modification was neutralization of the acid. The salt, sodium salicylate, was less unpleasant to swallow, but it was highly irritating to the stomach lining. Phenyl salicylate, the next substitute, passed unchanged through the stomach. In the small intestine, it was hydrolyzed to the desired salicylic acid, but phenol that is rather toxic, was also formed. Acetyl salicylic acid (aspirin) was then introduced.



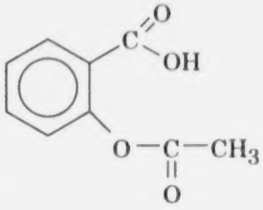
Salicylic Acid



Phenyl Salicylate
(salol)



Sodium Salicylate



Acetylsalicylic Acid

Thus a knowledge of the structure of drug molecules enables chemists to be more efficient when they design drugs. A knowledge of the structure of the drug molecule is not sufficient for an understanding of the molecular basis of the drug's action, however. It is also necessary for chemists to understand the structure of the molecules of the human body, of bacteria, and of viruses.

6. **Role of the Food and Drug Administration (FDA).** The FDA is responsible for approving the marketing of all new drugs sold in the U.S. The FDA also monitors drug use after approval. It can take up to ten years for a new drug to pass the rigorous program of safety and effectiveness for its intended use. First, evidence must show that the new drug has therapeutic activity in animals, that it shows promise for human use and that it appears to be safe for human testing. This is followed by human testing in patients with the disease and can involve thousands of patients to determine the drug's safety and effectiveness. Finally, the FDA examines all the evidence of safety and effectiveness and decides whether the drug will be approved for marketing. The FDA is very cautious so that people will be spared anguish and needless suffering.

7. **Drug interaction.** The interaction of drugs with each other to heighten each drug's effect is called synergism. The effects can be helpful or harmful. Physicians have succeeded in prolonging the lives of some cancer patients with combinations of drugs. When the drugs are given in combination, lower doses of each drug can be used, and the harmful side effects of chemotherapy reduced. On the other hand, alcohol (a depressant) increases the action of many antihistamines and tranquilizers (depressants) resulting in a superdespondent, dangerous combination.

8. **Drug manufacture.** Drug manufacture today is classified into five groups according to primary source. Plant extracts give alkaloids such as opium, quinine, atropine, and the precursors of steroid drugs. Animal extracts provide insulin and hormones. Vaccines and serums are prepared using biological sources. Fermentation is used for antibiotics such as penicillin, streptomycin, tetracycline, and steroid modification. Synthetic chemistry produces aspirin, tranquilizers, and antihistamines.

9. **Drug delivery.** Drugs can be administered through one of the following routes: oral ingestion, inhalation, injection, body orifices, skin application, skin patch, implants, and microsponges. Most drugs are taken orally. They dissolve in the stomach acid and enter the blood stream by absorption from the stomach or intestine. Inhaled drugs are rapidly absorbed into the bloodstream. Nasal decongestant sprays work by shrinking the nasal membranes. Injection also provides a direct route to the bloodstream, eliminating the possibility of undesirable taste or destruction by digestive juices. Drugs can also be administered in the form of eye drops, eye inserts, under the tongue tablets, and rectal and vaginal inserts. Smokeless tobacco users get their nicotine by stuffing tobacco between the gum and the cheek. Medications can be applied to the skin as ointments or as aerosol sprays. Skin patches are worn on a convenient area of the body as the drug is slowly absorbed into the bloodstream. One such skin patch releases scopolamine to the bloodstream and provides prolonged protection from the nausea and vomiting of motion sickness.

   Surgical implantation of a drug (pellet, reservoir, or pump) is another method of drug delivery. Contraceptive drugs have been implanted under the skin of a woman's upper arm. These implants, consisting of long, thin silicone rubber capsules that contain the drug, slowly release the contraceptive drug for about five years. Microsponges can be programmed to release drugs in response to pressure, time, or temperature changes. For example, a foot powder could release more antifungal drug with each step.

10. **Folk medicine**. This type of medicine is part of the culture of a geographical people, such as the American Indians. Folk medicine deals with the emotional needs of the patient that may be related to the patient's bodily ailments. The Native American medicine man often involved a patient's family and tribe so that personal conflicts were resolved while the patient also recovered physically. The tribal members sometimes offered gifts to the patient, and sometimes the ritual involved a family member with whom the patient had quarreled.

    Many practices of folk medicine are based on religion, superstition, or social customs. The medical (and religious) value of coca leaves was well recognized by the Incas. It was not until the 19th century that its analgesic property was recognized as due to cocaine. On the other hand, gold has no therapeutic value in the treatment of jaundice. The indigenous peoples of North America thought, erroneously, that "like cures like," and the color of gold matched that of the jaundiced person. With the various flora around them, they had a variety of remedies. They used foxglove as a remedy for fluid build-up in the legs resulting from heart failure. Today, the active ingredient in foxglove, digitalis, is a powerful cardiac drug. Native American medicines found their way into early folk practices of the white settlers. Unscrupulous peddlers claiming to have learned tribal formulas began to sell secret potions and elixirs. Many were nothing more than placebos and alcohol. Traveling road shows sold patent medicines such as Wigwam Tonic.

    There are over 200 indigenous drugs used by the Native Americans. Some of the common native North American plants that were (or still are) used medically are bloodroot (causes vomiting), podophyllum (for warts), tobacco (for toothache), goldenseal (an astringent), and mint (for fevers). Folk medicine is still practiced on some reservations.

11. **Holistic medicine**. Holistic medicine involves an understanding of the patient's whole situation. Emotional, spiritual, social lifestyle, and environmental factors are considered in the diagnosis and treatment of the disease. Many holistic approaches rely on psychology, and some practitioners emphasize muscular alignment through music, personal awakening, and physical manipulation. The importance of the mind in the treatment of physical ailments cannot be underestimated.

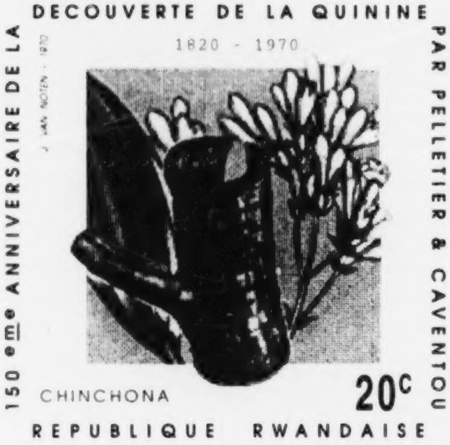
12. **Acupuncture**. This Oriental practice has been shown to relieve the symptoms of certain ailments or diseases. While its mechanism is not understood, its effectiveness is thought to be based on stimulus of endorphin synthesis in the body.

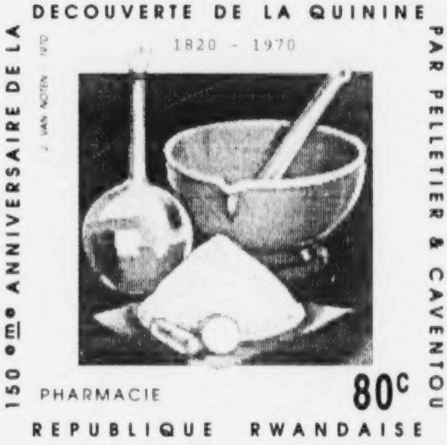
13. Have you recently had a headache? In North America, about 40 million pounds of aspirin is consumed per year. Since the average dose of two tablets is 1.7×10^{-3} mol, the total amount consumed corresponds to 59 billion headaches. That's enough to give anyone a headache!

14. The nicotine in the smoke inhaled from a pack of 20 cigarettes ranges from 2.0 to 40 mg!

Extensions

1. Consider these possible topics for development and discussion: herbal medicines, antibiotics, anticancer drugs, AIDS, computer designed drugs, and drug toxicity.
2. Research and debate the importance of vaccinating children against common childhood diseases such as mumps, measles, and polio. [Hint: Consider objections on religious grounds, or vaccinating if the disease is eliminated.]
3. Prepare an oral presentation about the life and contribution of the following medical scientists: Louis Pasteur, Joseph Pawan, Hippocrates, Robert Koch, and Alexander Fleming.
4. The stamps of Rwanda commemorate the discovery of quinine. What is the plant shown on the 20^c stamp? What chemical laboratory equipment is shown on the 80^c stamp? What are the insects shown on the 1^F and 25^F stamps? How does the disease affect an individual as shown on stamp 3^F? What is the underlying disease documented on these stamps? Who are Joseph Pelletier and Joseph Caventou as portrayed on stamp 70^F?


DECOUVERTE DE LA QUININE
1820 - 1970
150 eme ANNIVERSAIRE DE LA
PAR PELLETIER & CAVENTOU
J. VAN NOTEN - 1970
CHINCHONA
20c
REPUBLIQUE RWANDAISE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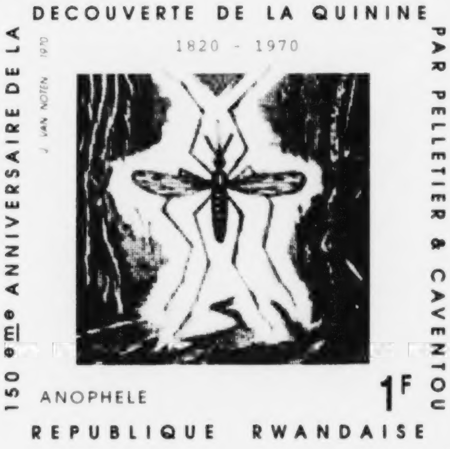
PAR PELLETIER & CAVENTOU
J. VAN NOTEN - 1970
PHARMACIE
80c
REPUBLIQUE RWANDAISE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PAR PELLETIER & CAVENTOU
J. VAN NOTEN - 1970
ANOPHELE
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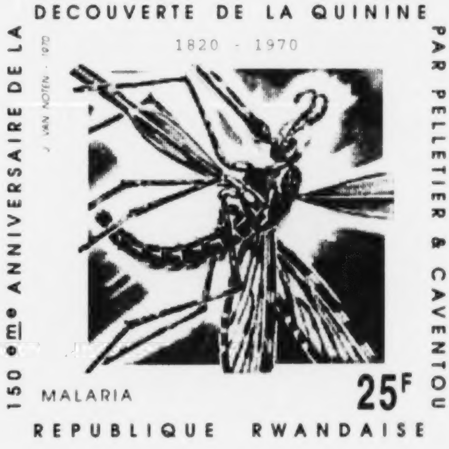
REPUBLIQUE RWANDAISE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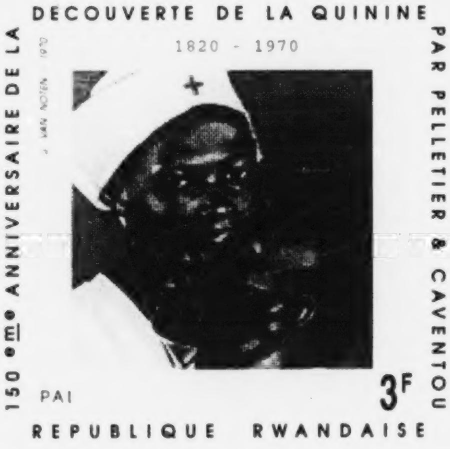
PAR PELLETIER & CAVENTOU
J. VAN NOTEN - 1970
MALARIA
25F
REPUBLIQUE RWANDAISE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1820 - 1970
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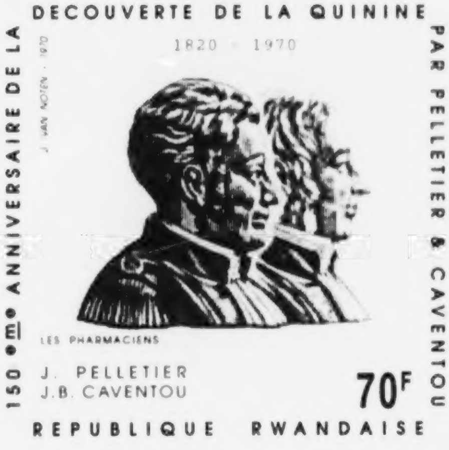
PAR PELLETIER & CAVENTOU
J. VAN NOTEN - 1970
PAI
3F
REPUBLIQUE RWANDAISE


DECOUVERTE DE LA QUININE
1820 - 1970
150 eme ANNIVERSAIRE DE LA
PAR PELLETIER & CAVENTOU
J. VAN NOTEN - 1970
LES PHARMACIENS
J. PELLETIER
J.B. CAVENTOU
70F
REPUBLIQUE RWANDAISE

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Module drafted by Philip Ogata, James Schreck, and Courtney Willis, the Colorado (North) team.

Burger, A. (Ed.). (1970). *Medicinal chemistry* (3rd Ed.). New York, NY: Wiley Interscience.

A three-volume set dealing with a study of the chemical mode of action of a variety of medicinal compounds and their interactions with other substances.

Committee on Chemistry and Public Affairs. (1977). *Chemistry in medicine: The legacy and the responsibility*. Washington, DC: American Chemical Society.

Hill, J. W. (1992). *Chemistry for changing times* (6th Ed.). New York, NY: Macmillan.

Chapters 22 and 23 provide information about chemical therapy and drugs.

Joesten, M. O., Netterville, J. T., and Wood, J. L. (1993). *World of chemistry: Essentials*. Philadelphia: Saunders Publishing Co.

Chemistry and Medicine is the title of Chapter 15.

Liska, K. (1990). *Drugs and the human body: With implications for society* (3rd Ed.). New York, NY: Macmillan.

A book for persons interested in examining high-use, high-abuse drugs in America, and the impact these drugs have on individuals and on society. The book can be used in health and drug education classes, public health courses, parent groups, and counselor training.

Martin, W. (1977). *Medical heroes and heretics*. Greenwich, CT: Devin–Adair.

This is the source (pp. 55–71) for "Jonas Salk and the Polio Vaccine." This book and *Men and Medicine* below tell the story of bold adventures in medicine. Of particular interest is the types of individuals who got involved in medical discoveries, who can and have followed revolutionary lines of thought for the benefit of humans.

The Merck index: An encyclopedia of chemicals and drugs, (11th Ed). (1989). Rahway, NJ: Merck.

A listing of chemicals including the trivial names, solubility, color, medical use, pharmacological activity, dose, and important or common side effects.

Selinger, B. (1989). *Chemistry in the marketplace* (4th Ed.). New York, NY: Harcourt, Brace, Jovanovich.

Chapter 9 is entitled *Chemistry in the Medicine Cabinet*.

Shippen, K. B. (1957). *Men of medicine*. New York, NY: Viking.

Steiner, R. P. (Ed.). (1986). *Folk medicine: The art and the science*. Washington, DC: American Chemical Society.

General interest book exploring the medical practices of non-Western cultures to establish a scientific basis for folk remedy successes. Explains why Western medical researchers look to folk medicine for new drugs, and looks at remedies from a variety of cultures and countries.

Taylor, J. B., and Kennewell, P. D. (1981). *Introductory medicinal chemistry*. New York, NY: Halsted.

This text describes the path of a drug from its formulation and entry into the human body, its distribution throughout the body, its interaction with active sites and its elimination.

Veenstra, T. (1993, September). Drinking and driving, *Chem 13 News*, p. 19.

Appendix

- **Transparency Masters**
    1. Drug Classifications
    2. Word Search
- **Humor**

Drug Classifications

Designation	Examples	Description
Controlled substances		Substances whose sale, distribution, and possession is controlled by the Drug Enforcement Administration
Schedule 1	Heroin, LSD, mescaline	Abused drugs with no medical use
Schedule 2	Morphine, amphetamines	Abused drugs with medical uses
Schedule 3	Valium, phenobarbital	Prescription drugs that are often abused
Over-the-Counter (OTC)	Antacids, aspirin, cough medicines	Available to anyone
Prescription drugs	Antibiotics	Available only by prescription
Unregulated nonmedical drugs	Ethanol, caffeine, nicotine	Available in beverages, foods, or tobacco

Word Search

L	R	B	Y	G	P	L	G	J	Y	B	B	L	T	H	J	U
T	V	N	V	D	O	W	S	E	N	I	E	F	F	A	C	W
E	L	V	I	L	T	R	W	V	H	Q	D	E	E	N	T	I
S	X	R	T	U	D	H	M	D	C	X	X	F	W	A	X	Z
T	C	Z	A	L	R	I	U	D	K	K	T	Q	T	L	R	Z
O	C	M	M	U	G	T	C	X	G	B	I	I	K	G	H	P
S	P	G	I	W	Y	V	X	A	S	D	I	O	R	E	T	S
T	E	C	N	A	R	E	L	O	T	M	Q	E	N	S	P	N
E	U	O	S	A	B	G	I	G	Z	N	Y	P	N	I	N	F
R	R	E	Y	K	U	M	R	A	M	Z	A	R	J	C	O	J
O	V	E	E	R	C	X	V	O	Z	U	P	I	I	L	A	M
N	Y	G	D	I	E	T	H	A	N	O	L	G	X	O	E	H
E	B	T	L	G	J	I	D	Y	E	N	F	V	T	Z	A	L

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Substance that reacts with excess stomach acid.
2. Common name for a substance that changes a physical or psychological function in the body.
3. Need of increasing amounts of a substance to experience the same initial effects.
4. Acetaminophen, ibuprofen, or acetylsalicylic acid, for example.
5. Benzoyl peroxide is the active antiseptic ingredient in ____ ointments.
6. These organic compounds are required in small amounts in the diet.
7. Stimulant in cola and coffee.
8. Birth control drugs belong to this class of organic compounds.
9. The amount of this drug is determined in the Breathalyzer test.
10. Anabolic steroids are synthetic derivatives of this natural compound.

Herman

"You're not getting enough Vitamin C."

Used by permission of Universal Press Syndicate

TANK McNAMARA
SPORTS
HIGH SCHOOL PHENOM NIXES COLLEGE FOOTBALL FOR MED SCHOOL
MICHIGAN STATE. USC. NOTRE DAME. HE COULD HAVE PLAYED ANYWHERE HE WANTED
LOOK WHAT YOU'VE DONE TO YOUR FATHER.
BUT DAD! I'LL BE A DOCTOR. I'LL HEAL THE SICK. ISN'T THAT IMPORTANT?
MILLAR/HINDS
BIG HAIRY DEAL! CAN A FATHER TURN ON THE TV AND SAY 'THAT'S MY BOY, HEALING THE SICK IN THE ROSE BOWL'?

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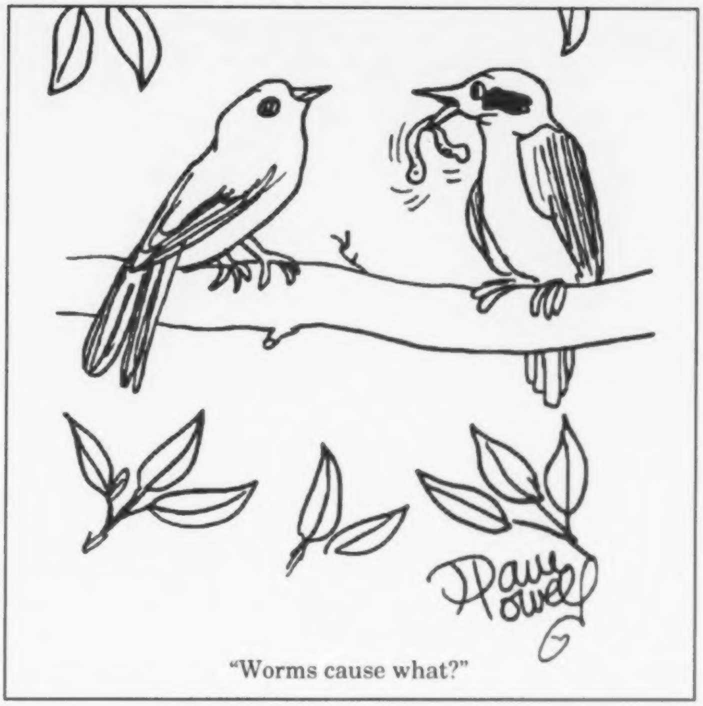
GLONCO ASPIRIN MARKETING PLAN 1981-2
NEW LABEL
2-ethanoyloxybenzenecarboxylic acid
"IUPAC or no - you can't get that onto a 5g bottle"

CHEM 13 NEWS, February 1982, p. 2. Reprinted with permission.

"Would you mind if I ask just what you're being treated for?"

CHEMTECH, February 1980, p. 77. © American Chemical Society. Reprinted with permission.



"Worms cause what?"

CHEMTECH, April 1980, p. 214. © American Chemical Society. Reprinted with permission.

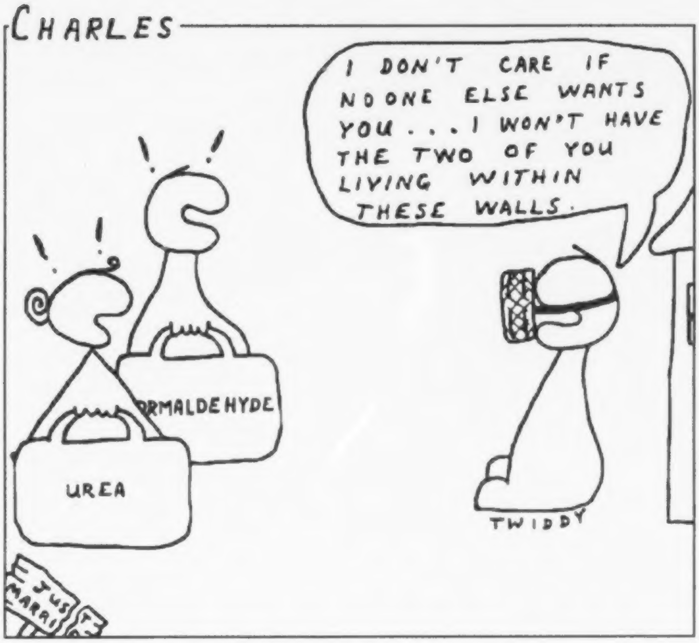
458

WELL I GUESS THEY REALLY DID MEAN IT WHEN THEY SAID "MAY RESULT IN SIDE EFFECTS IF TAKEN INTERNALLY"

CHEM 13 NEWS, September 1981, p. 3. Reprinted with permission.

ONDER
DRUG
OSEELOX
NEW
UWE
CURES HAYFEVER, HEAD COLDS, CONGESTION, COUGHING, SORE THROATS AND IMPROVES TV RECEPTION

CHEM 13 NEWS, March 1979, p. 7. Reprinted with permission.


CHARLES
I DON'T CARE IF NO ONE ELSE WANTS YOU . . . I WON'T HAVE THE TWO OF YOU LIVING WITHIN THESE WALLS.
RMALDEHYDE
UREA
TWIDDY
JUS MARRI

CHEM 13 NEWS, January 1985, p. 9. Reprinted with permission.

A SourceBook Module

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$$6.02 \times 10^{23}$$

THE MOLE

ChemSource

Instructional Resources for Preservice and
Inservice Chemistry Teachers

Topic Overview

CONTENT IN A NUTSHELL

The mole concept pervades all of chemistry. Since most quantitative chemical calculations are based on the mole, an understanding of the mole is essential to the study of chemistry. An understanding of how the mole relates to mass, number of entities (atoms, molecules, ions, *etc.*) and volume of a gas is included in this module. Formulas are most often interpreted in terms of moles rather than atoms, molecules or formula units (see *Language of Chemistry* section) since chemical reactions are generally carried out on a macroscopic scale.

The SI definition of mole is: "... the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kg of carbon 12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles."

Chemists use the mole (symbolized *mol*) to express amount of substance (elements, compounds, ions, electrons, *etc.*). Avogadro's number (6.02×10^{23}) is the number of entities in one mole of a substance. Because it is easier to weigh large numbers of particles than to count them, chemists generally relate moles of a substance to mass rather than to the number of particles. The molar mass (mass of one mole) of a substance is the sum of the relative atomic masses (in grams) of the elements in a formula unit of the substance. Avogadro's number of formula units of a substance has a mass equal to the molar mass of the substance.

The subscripts in a formula can be interpreted as the number of moles of the element present in a mole of the compound. Calculations involving percent composition of a compound and empirical formula involve the mole concept. (The relationship of moles to stoichiometry is the subject of another *SourceBook* module.)

This topic lends itself to a historical presentation (see *History* section).

PLACE IN THE CURRICULUM

Since it is the basis for quantitative chemistry, the mole is usually introduced early in the course. Because it requires abstract reasoning, the mole is a challenging concept for many beginning students. If students have a poor mathematical background, it may be desirable to postpone introduction of the mole concept, perhaps until after a discussion of atomic structure and bonding.

CENTRAL CONCEPTS

1. One mole of a substance represents Avogadro's number (6.02×10^{23}) of units of that substance.
2. The amount of a substance (expressed in moles) is related to the mass of substance, and for a gaseous substance, to its volume.
3. The mole is the basis of quantitative chemistry (percent composition, empirical and molecular formula determinations).

RELATED CONCEPTS

1. Mass, volume
2. Formulas (empirical and molecular)
3. Atoms, molecules, formula units

4. Percent
5. Accuracy and precision
6. Gas behavior (particulate nature of matter, relationship of volume to number of molecules of gas)
7. Stoichiometry

RELATED SKILLS

1. Measurement
2. Exponential numbers
3. Significant figure manipulation
4. Problem solving strategies (dimensional analysis, *etc.*)
5. Algebra
6. Use of balance
7. Volume measurements
8. Use of burner
9. Use of tongs to handle crucibles

PERFORMANCE OBJECTIVES

After completing their study of the mole concept, students should be able to:

1. define mole in terms of mass and number of entities.
2. explain the difference between the terms *mole* and *molecule*.
3. explain why chemists find it convenient to express the quantity of a substance in moles (rather than mass, volume, number of entities, or some other unit).
4. calculate the molar mass of a substance, given its formula.
5. calculate moles, mass or number of entities (atoms, molecules, formula units, *etc.*), given appropriate data.
6. calculate moles, mass or volume of a gas sample at STP, given appropriate data.
7. determine percent composition of a substance, given its formula.
8. determine empirical formula, given the percent composition of a substance or the relative masses of the elements in the substance.
9. determine the molecular formula of a substance, given its empirical formula and other appropriate data.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Understanding the Mole

[Adapted from: Laboratory Manual accompanying Chemical Principles by Masterton and Slowinski. Modifications by Norma Mackenzie of Charlotte Country Day School, Charlotte, North Carolina.]

Introduction

The relative mass of an object is how many times more massive the object is than a standard object. The atomic masses of atoms are all relative masses. They can be considered relative to any particular element. Historically, both oxygen and carbon have served as the reference standard. For our purposes we can also consider atomic masses relative to the least massive element—hydrogen, with an atomic mass of approximately one. Fluorine, with a relative mass of 19, is 19 times more massive than hydrogen, *etc.* In this laboratory exercise you deal with the relative masses of beans. Then you will be asked to draw a parallel to the atomic masses of elements.

Purpose

To develop an understanding of the mole concept and molar masses of elements through an analogy with a model system.

Safety

Just don't spill the beans!

Procedure

Part I

1. Obtain a numbered plastic cup. Record the number of the cup; be sure to use the same cup during the entire activity.
2. Record the mass of your cup to the nearest 0.01 g.
3. Count out exactly 100 beans of one type. Discard any beans that differ greatly from an average bean. If you fail to do this, your results will not be accurate.
4. Weigh the beans; record their mass to the nearest 0.01 g.
5. Repeat Steps 3 and 4 for each type of bean provided.

Calculations

6. Calculate the mass of 100 beans by subtracting the mass of the plastic cup from the mass of the plastic cup + 100 beans.
7. Calculate (do not weigh) the mass of one bean of each type. Record the value in the data table. *[NOTE: "Calculate" means to take the total mass of 100 beans and divide by 100 rather than weighing one particular bean.]*
8. Determine the relative mass of each type of bean.

$$\text{Relative Mass} = \frac{\text{Average mass of one bean}}{\text{Average mass of the lightest type of bean}}$$

9. Calculate the number of beans in one relative mass of each bean. Do this by dividing the average mass of one bean into the relative mass.

$$\text{Number of beans in one relative mass} = \frac{\text{Relative mass}}{\text{Average mass of one bean}}$$

10. Check your calculated results in Step 9 by following these steps:
    a. Weigh the empty plastic cup again and record its mass.
    b. Determine the sum of the relative mass of one type bean and the mass of the plastic cup.
    c. Place the plastic cup on the balance pan and add beans of that type until the balance contains one relative mass of that type bean. (The mass should be that calculated for the cup plus one relative mass.)
    d. Count the beans. Record this as the measured number of beans in one relative mass.
    e. Pour the beans into a pile. Retain your separate piles of relative masses of beans. You will answer questions about them later.
    f. Repeat for each type bean.

Data Analysis and Concept Development

Cup Number ________

Mass of empty cup before activity ________ g

Mass of empty cup after activity ________ g

	Bean 1	Bean 2	Bean 3	Bean 4
Mass of 100 beans plus cup (g)				
Mass of 100 beans (g)				
Average mass of one bean (g)				
Relative mass of beans				
Calculated number of beans in one relative mass				
Measured number of beans in one relative mass				

Implications and Applications

1. What did you find out about the number of beans in one relative mass? How do your calculated values compare to your measured values?
2. How many times larger is the lima bean relative mass than the lentil bean relative mass? How does this relate to the number of beans in the relative mass?
3. In a very logical statement, explain why there are always the same number of beans in one relative mass. Think very hard about this one.
4. Compare the volume of relative mass piles. Are they the same? Why or why not?
5. a. What is the average mass of the lightest bean?
   b. What is the relative mass of the lightest bean?
6. Among the elements, hydrogen has the least massive atoms—an atom of hydrogen has an average mass of 1.66×10^{-24} g. This is very small, but remember it is only *one* atom! What is the relative mass of hydrogen if it is the least massive element?

Part II

Examine the beakers of elements and compounds on display. Each beaker contains one mole of a particular substance. Record information on the chart below.

Substance	Volume of one mole	Mass of one mole	Smallest unit of substance (atom or molecule?)
Sucrose ($C_{12}H_{22}O_{11}$)			
Carbon (C)			
Tin (Sn)			
Zinc (Zn)			
Aluminum (Al)			
Copper (Cu)			
Water (H_2O)			

7. a. Which substance occupies the largest volume?
   b. Which substance occupies the smallest volume?
8. a. One mole of which substance has the largest mass?
   b. Which substance has the most massive individual particles?
   c. Why *must* the answers to Questions 14a and 14b be the same?
9. Why do equal amounts (in moles) of different elements and compounds have different masses even though they have the same number of particles?
10. Why do equal amounts (in moles) of elements or compounds occupy different volumes?
11. Describe the fastest way to measure one relative mass of beans.
12. Describe the fastest way to measure out one mole of beans.

Part III

Below is a chart reporting the average masses of individual atoms. Calculate the relative mass of each element and record it in the chart. Then look up the molar mass (atomic mass) of each element on a Periodic Table and record it in the table.

Atom	**Mass of one atom (g)**	**Mass relative to hydrogen (calculate)**	**Atomic mass**	**Number of atoms in a relative mass (g) (calculate)***
Hydrogen	1.66×10^{-24}			
Carbon	2.00×10^{-23}			
Iron	9.30×10^{-23}			
Aluminum	4.49×10^{-23}			
Zinc	1.08×10^{-22}			
Lead	3.44×10^{-22}			
Copper	1.05×10^{-22}			

* Although this calculation works with a relative mass of hydrogen of 1.00 as its basis, atomic masses are actually calculated as relative to a particular type of carbon atom viewed as exactly 12.00.

13. Comment on how the atomic masses found on the Periodic Table compare to the relative masses you calculated.
14. What are atomic masses, and how are they determined?
15. What did you find out about the number of atoms of each element in one relative mass?
16. Whose name is given to the number of atoms in the relative mass?
17. One atomic mass unit (u) is the approximate mass of a proton or a neutron. This mass is equal to 1.66×10^{-24} g. How many atomic mass units are in one gram?
18. If an atom has a mass of 197 u, find the mass (in g) of a mole of these atoms.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Understanding the Mole

Major Chemical Concepts

Molar masses are derived from relative masses (see SI definition of mole in *Content in a Nutshell*). Molar masses of different substances have different masses and volumes. Each relative mass contains the same number of particles.

Level

This activity may be used with first-year high school chemistry students in basic, general, or honors levels.

Expected Student Background

Students should know how to use a balance. They should have a scientific calculator and be able to use and understand the calculator's exponential function. It would be helpful if students were acquainted with the concepts of significant figures, and knew that the last digit is an estimated number and that some variation is expected in this value.

Time

This is a two-day activity, assuming 45 to 55-min class periods. *Part I* is completed on the first day. *Part II* and *Part III* are done on the second day. Students turn in data tables, calculations, and answers to questions at the close of the second day.

Safety

1. No safety concerns are associated with this activity; students do not need to wear protective goggles, unless strict school regulations require them *whenever* students are at the laboratory bench.
2. The "one mole" of elements and compounds should be covered to prevent spilling. There could be a physical hazard of slipping on beans if many of them are spilled on the floor.

Materials (For 24 students working in pairs)

Nonconsumables

Covered containers for beans
12 Numbered plastic drink cups
48 Zip-closure bags (optional)
6 Beakers, 50-mL (with graduations to hold one-mole amounts of elements and water)
Beaker, 800-mL (with graduations; to hold one mole of sucrose)

Approximate quantities of beans:

Lentil beans, 1 bag (3 oz.)
Lima beans, 2 large bags (2 1/4 lb.)
Navy beans, 1 bag (8 oz.)
Pinto beans, 1 large bag (1 1/4 lb.)

One mole of each substance in powdered or granular form, except for water:

Water, 18 mL (18 g)
Aluminum, 27 g
Copper, 63.5 g
Sucrose (table sugar), 342 g
Carbon, 12 g
Tin, 119 g
Zinc, 65 g

Advance Preparation

First Day: Number the plastic cups. Cups may differ in mass by as much as one gram; each group should continue to use the same weighed cup. Place beans in a closable container that is easy for students to get to. If desired, approximately 120 beans of each type can be weighed into zip-closure bags (lentils - 8 g, navy beans - 208 g, pinto beans - 48 g, lima beans - 120 g per zip-closure bag). This will save student time.

Second Day: Place one mole of each of the specified elements, sucrose, and water in separate beakers. Label each one, cover each beaker with plastic wrap and put a rubber band on it. This prevents spillage and evaporation of water. Place these beakers around the laboratory. (These samples can be stored covered and reused indefinitely - except for water, which will evaporate.)

Pre-Laboratory Discussion

Draw students' attention to the Periodic Table. They will have seen the table in the classroom for several weeks—and in previous courses. They are usually curious about what it means and why it is arranged the way it is. You might ask them to spot any regularities in the chart. Among other things, they should be able to see that atomic numbers always increase across a row. Atomic *masses* usually increase—but not always. They also are curious about the decimal values in the atomic masses. Point out that a hydrogen atom is the lightest atom and that, for example, a gold atom weighs about 197 times more than a hydrogen atom. Students are curious how these numbers were determined, and how Avogadro's number was determined. Explain to students that by doing this activity, they will be able to understand, in part, how these things came about.

An analogy could also be discussed with students. A dozen golf balls would not have the same mass as a dozen ping pong balls. We could find the relative mass of the golf balls if we weighed a dozen ping pong balls and a dozen golf balls, and divided by the smaller mass. This would tell us not only how many more times massive a dozen golf balls were than a dozen ping pong balls, but also how many times more massive one golf ball is than one ping pong ball.

Teacher-Student Interaction

1. Move from group to group, checking to see that students understand the instructions. It is best to guide students by responding with questions that lead them to correct answers.
2. The concept of relative mass (Question 8 in *Part I Calculations*) may be a difficult concept for students. The concept should be clarified when the calculated value is verified experimentally (Question 10 in *Part I Calculations*).
3. Insure that students understand the relationship of *Part II* to *Part I*. (Since individual beans can be handled, they provide a concrete analogy. Since atoms and molecules cannot be seen, one must visualize them mentally. The calculations involving beans in *Part I* are analogous to those involving elements in *Part II*.)

Anticipated Student Results

Cup Number X

Mass of empty cup before activity 12.15 g

Mass of empty cup after activity 12.15 g

	Bean 1 (Lentils)	Bean 2 (Navy)	Bean 3 (Pinto)	Bean 4 (Lima)
Mass of 100 beans plus cup (g)	18.16	28.65	52.55	113.15
Mass of 100 beans (g)	6.01	16.50	40.40	101.00
Average mass of one bean (g)	0.0601	0.165	0.404	1.01
Relative mass of beans	1.00	2.75	6.72	16.80
Calculated number of beans in one relative mass	16.60	16.70	16.70	16.80
Measured number of beans in one relative mass	17	17	17	17

These values are typical student values. Lima beans vary greatly in size, thus having the largest uncertainty.

Answers to Implications and Applications

1. The calculated number of beans in one relative mass stayed the same at 16.7 ± 0.1 bean. The measured number stayed constant at 17 ± 1 bean.
2. The lima bean relative mass is about 17 times larger than the lentil bean relative mass. There are 17 beans in a relative mass. These values are the same.
3. The relative mass is the ratio of the mass of one type of bean to the mass of another type of bean. This mass ratio insures that when we weigh beans in this mass ratio, we must obtain the same number of beans. (Since a lentil bean is only 1/17 as massive as the most massive bean measured—the lima bean—there must be 17 beans in a relative mass.)
4. The volumes of the relative mass piles are not the same. Even though each pile has the same number of beans, they have different sizes.
5. The average mass of the least massive bean is 0.0601 g. The relative mass of the least-massive bean is 1.00.
6. If it is the least massive element, its relative mass should be 1.00.

Part II

Substance	Volume of one mole	Mass of one mole	Smallest unit of substance (atom or molecule?)
Sucrose ($C_{12}H_{22}O_{11}$)	450 mL	342.0 g/mol	Molecule
Carbon (C)	6 mL	12.01 g/mol	Atom
Tin (Sn)	23 mL	118.7 g/mol	Atom
Zinc (Zn)	20 mL	65.4 g/mol	Atom
Aluminum (Al)	18 mL	27.0 g/mol	Atom
Copper (Cu)	12 mL	63.5 g/mol	Atom
Water (H_2O)	18 mL	18.0 g/mol	Molecule

Note: These are not molar volumes, but the approximate volumes occupied by 1 mole of each substance, *eg.* crystalline sucrose.

7. Sucrose occupied the largest volume. Carbon occupied the smallest volume.
8. Sucrose had the largest molar mass and the most massive individual particles. These answers must be the same because all beakers contained the same number of individual units.
9. One mole of various entities have different masses because their individual particles have different masses, just as different kinds of beans have different masses.
10. One mole of various entities occupies different volumes because their individual particles have different volumes, just as piles of relative masses of beans have different volumes. (The volumes of solids that are not a single crystal, however, will not be directly related to the volume of the atoms or particles.)
11. The fastest way to obtain a relative mass of beans would be to count the beans. The fastest way to obtain a mole of beans would be to weigh them. (At least in principle. The mass of a mole of beans would be incredibly large—on the order of 10^{22} g.)

Part III

Atom	Mass of one atom (g)	Mass relative to hydrogen (calculate)	Atomic mass	Number of atoms in a relative mass (g) (calculate)*
Hydrogen	1.66×10^{-24}	1.00	1.008	6.02×10^{23}
Carbon	2.00×10^{-23}	12.0	12.01	6.03×10^{23}
Iron	9.30×10^{-23}	56.0	55.85	6.02×10^{23}
Aluminum	4.49×10^{-23}	27	26.98	6.01×10^{23}
Zinc	1.08×10^{-22}	65.1	65.45	6.03×10^{23}
Lead	3.44×10^{-22}	207	207.2	6.02×10^{23}
Copper	1.05×10^{-22}	63.3	63.45	6.03×10^{23}

* calculated using columns 2 and 3

12. All atomic masses agree with the relative masses to three significant figures. (Some variation in the last significant digit is always expected.
13. Atomic masses are relative masses. They are calculated relative to some reference atom. *NOTE: Molar masses of elements are accurately known*. The number of carbon atoms in a unit cell is determined precisely by X-ray crystallography, and the density of carbon is determined. Using these precise measurements, all other atomic masses are taken relative to the carbon-12 isotope as exactly 12.
14. The number of atoms in a relative mass is constant at 6.02×10^{23}.
15. This is Avogadro's number.
16. There are 6.02×10^{23} atomic mass units in one gram.
17. A mole of these atoms would have a mass of 197 g. *(TEACHER NOTE: This is a gold atom.)*

Post-Laboratory Activities

At this point, students can begin calculations regarding molar masses of different molecules. Worksheets where "dozens" are discussed along with the concept of the mole should be provided. Throughout the year, when the mole concept or atomic masses of elements are discussed, remind students of this bean activity. Students usually make the connection easily and have a model to help them understand these ideas.

Extensions

1. Ask students to weigh out 100 grains of rice, and then recalculate their relative masses. They could then rethink some of their answers about why relative masses contain the number of items they do.
2. Students might also like to apply this same idea to other familiar objects—for example, game balls (baseballs, soccer balls, bowling balls, footballs, golf balls, ping pong balls, *etc.*) They could weigh individual balls or dozens of balls and prepare a table with names, symbols, and relative masses. Since bowling balls come in 12-pound, 16-pound sizes (and other sizes), the idea of isotopes could be discussed. The concept of a weighted average relative mass could be developed. The concept of isotopes (or relative masses) could be developed with paper clips, nails, styrofoam balls, or anything with relatively constant mass and several types of individual items.

Assessing Laboratory Learning

1. The laboratory data sheets should be collected and graded. Most students will identify any large errors in measurement of relative masses because they will not fit with other answers.
2. This is an opportunity to use cooperative learning and let groups of students discuss their ideas and give consensus answers to some of the more difficult questions. A group grade can then be given. Students appreciate this communication on discussion questions; cooperative learning helps foster a positive feeling about this process. It is far better than obtaining 30 papers with identical answers to discussion questions that represented original thoughts of only a few students.

3. Questions on worksheets as well as on tests focusing on concepts developed in this learning activity should be posed throughout this module and throughout the year. Clarity of thought on this pivotal concept should be evaluated in as many contexts as possible. (The worksheet on "dozens" uses familiar English units, so that students can work with calculations analogous to the mole concept using more familiar units. If desired, metric units could be substituted. A suitable worksheet follows.)

Answers to Worksheet on Dozens and Moles

Part I

1. (192 lb bowling balls) / (0.24 lb ping pong balls) = **8.0 x 10^2 times**
2. (1.44 lb golf balls) / (0.24 lb ping pong balls) = **6.0 times**
3. (0.24 lb/1 doz) x (1 doz/12 balls) = **0.020 lb**
   0.020 lb x (16 oz/1 lb) = **0.32 oz**
4. 1.44 lb x (1 doz/12 balls) = **0.120 lb**
   0.120 lb x (16 oz/1 lb) = **1.92 oz**
5. 0.040 lb x (1 doz/0.24 lb) x (192 lb/1 doz) = **32 lb**
6. 180 balls x (1 doz/12 balls) = **15 doz**
   15 doz x (1.44 lb/1 doz) = **21.6 lb**
7. 48 lb x (1 doz/192 lb) x (12 balls/1 doz) = **3.0 balls**
8. 20,000 balls x (1 doz/12 balls) x (1.44 lb/1 doz) = **2.40 x 10^3 lb**

Part II

Element	Mass of one mole
Helium	4.00 g/mol
Carbon	12.0 g/mol
Gold	197 g/mol

1. (197 g/mol gold) / (4.00 g/mol helium) = **49.3 times**
2. (4.00 g/1 mol) x (1 mol/6.02 x 10^{23} atoms) = **6.64 x 10^{-24} g/atom**
   6.64 x 10^{-24} g x (1 u/1.66 x 10^{-24} g) = **4.00 u**
3. (12.0 g/1 mol) x (1 mol/6.02 x 10^{23} atoms) = **1.99 x 10^{-23} g/atom**
   1.99 x 10^{-23} g x (1 u/1.66 x 10^{-24} g) = **12.0 u**
4. 0.50 g x (1 mol/4.00 g) x (197 g/1 mol) = **25 g**
   (Using solution to Question 1: 0.50 g x 49.3 = **25 g**)
5. 3.01 x 10^{24} atoms x (1 mol/6.02 x 10^{23} atoms) = **5.00 mol**
   5.00 mol x (12.0 g/1 mol) = **60.0 g**
6. 25 g x (1 mol/197 g) x (6.02 x 10^{23} atoms/1 mol) = **7.6 x 10^{22} atoms**
7. 3.01 x 10^{19} atoms x (1 mol/6.02 x 10^{23} atoms) x (197 g/1 mol) = **9.85 x 10^{-3} g**

Name ______________________ Period _____ Date ________

Worksheet on Dozens and Moles

Part I. The following are masses of one dozen game balls

Type of Ball	Mass of one dozen
Ping pong	0.24 lb (110 g)
Golf	1.44 lb (654 g)
Bowling	192 lb (87.2 kg)

1. How many times more massive is a bowling ball than a ping pong ball?

2. How many times more massive is a golf ball than a ping pong ball?

3. How much does one ping pong ball weigh in pounds? In ounces?

4. How much does one golf ball weigh in pounds? In ounces?

5. You have 0.040 lb (18 g) of ping pong balls. How many pounds of bowling balls must you obtain to have the same number of each type of ball?

6. How many dozen golf balls are present in 180 golf balls?

   How much would these golf balls weigh in pounds?

7. If you had 48 pounds of bowling balls, how many bowling balls would you have?

8. You must ship 20,000 golf balls. You do not have time to count them. It is faster to weigh them. How many pounds of golf balls must you ship?

Part II

Look up the atomic masses for helium, carbon, and gold to answer the following questions.

Element	Mass of one mole
Helium	
Carbon	
Gold	

1. How many times more massive is a gold atom than a helium atom?

2. What is the average mass of one helium atom in grams?

   What is its mass in atomic mass units (u)? (1 u = 1.66×10^{-24} g)

3. What is the average mass (in grams) of one carbon atom?

   In atomic mass units?

4. You have 0.50 g of helium atoms. How many grams of gold atoms must you obtain to have the same number of atoms of each?

5. How many moles of carbon atoms are there in 3.01×10^{24} atoms of carbon?

   How many grams of carbon is this?

6. If you have 25 g of gold, how many atoms of gold do you have?

7. How many grams of gold would you have to obtain to have 3.01×10^{19} atoms of gold?

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: Percent Composition of Magnesium Oxide

Introduction

The Law of Definite Composition is introduced early in general chemistry as a part of exploring differences and similarities between compounds. Proust, a French chemist, was one of the first to state this principle. Using this principle, chemists in laboratories and industry are able to determine with high precision the amounts of each substance needed to make a compound.

Purpose

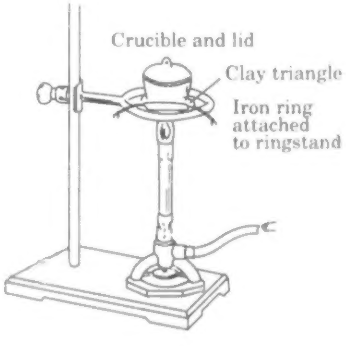
This activity is designed to support the concept of a definite percent by mass of each element in the binary compound magnesium oxide.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Do not touch the hot crucibles. Hot porcelain and cold porcelain look the same.
3. Follow proper procedures when lighting burners.
4. Keep your hair pulled back away from your face so it will not come close to the burner flame. Hair ignites easily, especially if hair spray is used.
5. Handle the Mg ribbon with tongs as much as possible. The ribbon is usually sharp along its edges from cleaning; it can cut easily. Do not look at the magnesium while it is burning.
6. When handling crucibles, hold a piece of wire gauze up close under the crucible while moving the crucible from the clay triangle to the balance, *etc.* This will save many crucibles and prevent hot porcelain from shattering and causing burns.
7. Dispose of materials as your teacher directs.
8. Thoroughly wash your hands before leaving the laboratory.

Procedure

1. Heat an empty crucible (with cover). Begin heating with a cool flame and gradually increase the temperature. Heat with a hot flame for 2-3 min. Allow to cool enough to handle with tongs. Weigh and record. Be careful not to place the crucible on counter tops, *etc.* that may melt or burn.
2. Place a coil of cleaned Mg ribbon provided for you in the crucible. (Your teacher may direct you to cut the Mg ribbon into small pieces to speed up the reaction.)
3. Weigh the crucible and Mg ribbon. Record.
4. Place the crucible and Mg ribbon in the clay triangle.
5. Heat the crucible and Mg ribbon in stages for 10-15 min. The clay triangle should glow red hot during this time.
6. Open the crucible with tongs to allow more air to enter while continuing to heat. Heat for 10 min more.



7. Remove the crucible and contents from the clay triangle and place it on a piece of wire gauze. Allow to cool about 5 min or until you can comfortably touch the crucible with a finger. *Be Careful!* Hold the back of your hand near the crucible to feel the heat.
8. Add 2 mL water to the crucible contents. (Use distilled water, if available.) Cover and return the crucible to the clay triangle.
9. Heat gently by moving the burner flame back and forth under the crucible for about 2 min. Then heat strongly for about 5 min to insure dryness.
10. Remove the crucible from the clay triangle and place it back on the wire gauze. Weigh when cool enough to handle. Record.
11. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

Data Chart

1. Mass of empty crucible and cover ________
2. Mass of crucible, cover, and Mg ribbon ________
3. Mass of Mg ________
4. Mass of crucible, cover, and contents after heating ________
5. Mass of contents (mostly MgO, we hope!) ________
6. Mass of oxygen combined with Mg ________

Observations

Be sure to note colors of the Mg ribbon and the crucible contents during the activity. Also note any odor you may have encountered when water was added.

Analysis of Data

1. Using the mass of the contents (mostly MgO) and the mass of the magnesium ribbon you used, calculate the percent magnesium in magnesium oxide. Using the mass of oxygen and mass of contents, calculate the percent oxygen in magnesium oxide.
2. Assume the formula for magnesium oxide is MgO. Calculate the theoretical mass percent of Mg and O. Molar masses are:

   Mg = 24.305 O = 15.9994 MgO = 40.304
3. Compare your data to theoretical values. Suggest reasons why your values might not match theoretical values.
4. Write a balanced equation for the primary reaction between Mg and O_2.

Implications and Applications

1. Why is it necessary to preheat the crucible?
2. Why was it necessary to open the crucible lid to allow more air to enter during the reaction?
3. Why was water added to the contents?
4. What changes in the procedure could have been made, if time allowed, to insure that the Mg ribbon had completely reacted?
5. How could you explain Mg mass percent values that are too high and those that are too low?
6. Explain how you could use this general laboratory procedure to identify a compound if you know the elements that compose it.
7. What effect would using unclean Mg ribbon have on your results?

*8. A student forgets to add water at the end of the procedure. What effect would this possibly have on the student's results? Do you think your equipment would be precise enough to detect this error?

*Optional

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: Percent Composition of Magnesium Oxide

Major Chemical Concept

The activity illustrates the importance and usefulness of the Law of Definite Composition, emphasizes the mole concept, and involves calculations of empirical formulas.

Initial emphasis is on calculating percent composition; this is relatively easy for students to understand and calculations are straightforward. The determination of empirical formula and illustration of the utility of the mole concept are both clearer when pooled data for the entire class are used. Students calculate moles Mg and moles O from their experimental data. A plot of moles of Mg *vs.* moles of O for class data gives a graph with the expected slope of about 1.

Level

General and honors. Also possibly basic, with enough teacher guidance.

Expected Student Background

Students should be able to calculate simple percent values and deal with molar mass. They should be familiar with standard laboratory procedures. Additional background is optional, such as applications of oxidation-reduction concepts to this laboratory activity.

Time

This activity can be completed in one period if the pre-laboratory briefing is provided in a previous class period. If time becomes a concern, you can do the final weighing for students or save the final weighing until the next day, particularly if you have a drying oven to keep crucibles dry.

Safety

Read *Student Version* considerations.

Materials (For 24 students working in pairs)

Nonconsumables

Balance (to nearest 0.001 g if possible)
12 Burners
12 Clay triangles
12 Crucibles and lids
12 Crucible tongs
12 Graduated cylinders, 10-25 mL
12 Ringstands
12 Rings
12 Strikers (or other means to ignite the gas)
12 Wire gauze

Consumables

Distilled water, optional
Magnesium ribbon, Mg, 2.4 to 4.8 g

Advance Preparation

1. All equipment should be readily available to students. Having needed equipment in plain view at laboratory stations saves considerable student work time. In general, check equipment ahead of time.

2. Remove the oxide coating from the Mg ribbon by slightly sanding. Cut it in lengths with masses between 0.200 g and 0.400 g before the activity begins.
3. Check the balances to insure they work properly.
4. If distilled water is used, consider providing it in water bottles at each station.
5. You may wish to pose some problems (*e.g.*, percent composition, mole problems, *etc.*) for students to solve during the time samples are cooling.

Pre-Laboratory Discussion

1. Demonstrate any procedural skills students have not seen before, such as proper handling of crucibles with tongs and the lighting of a burner. It is important to show the set up so students will be able to quickly assemble it themselves.
2. Give students thorough instructions regarding safety. Warn students that cool and hot porcelain look the same; encourage caution when handling the crucibles. Holding a piece of wire gauze under the crucible when moving it from place to place will save some crucibles from rapid increases in entropy.
3. Explain that under the conditions of this activity magnesium reacts with nitrogen gas in air as well as with oxygen gas. The contents should be as free as possible of magnesium nitride, Mg_3N_2. This is accomplished by adding water to convert magnesium nitride into ammonia and magnesium oxide. A faint odor of ammonia, NH_3, may be detected by some students:

$$Mg_3N_2(s) + 3H_2O(l) \rightarrow 3MgO(s) + 2NH_3(g)$$

4. Students should be asked about procedure details such as opening the lid *[to allow more air in]*. They should also be asked why it is necessary to heat the Mg ribbon strongly until the clay triangle and possibly the crucible itself glow red hot *[to insure complete reaction and to dry the MgO after addition of water]*.
5. Insure that students understand how the collected data relate to the calculations they will perform.
6. You may decide to supply problems for students to solve or provide some other activity to keep students busy during the time samples are cooling. If so, explain the nature of the assignment during the pre-laboratory orientation.

Teacher-Student Interaction

1. Move from group to group, insuring proper set ups and safe lighting of burners. Do not hesitate to assist in the lighting of burners at first. This process should be monitored closely.
2. Since the crucibles will be heated for long periods of time, use this opportunity to further discuss the reactions with individual groups. Consider providing them with a list of questions you will expect them to answer after the activity so they can discuss them with each other or with you.
3. Circulate and be sure students make good observations when they open the crucible at different points in the procedure. They will note color changes.
4. Do not be alarmed if the final product is not pure white, as MgO should be. The gray coloration can be due to several reasons, but largely to impurities in the crucible and water. Students may note that this gray color is not the "expected" color of pure MgO. Invite them to suggest reasons. Actual laboratory data from this activity, however, usually do not indicate that this discoloration leads to any problems in the calculated results.

Anticipated Student Results

Here are actual data from one student's laboratory report.

1.	Mass of empty crucible and cover	27.225 g
2.	Mass of crucible, cover, and Mg ribbon	27.568 g
3.	Mass of Mg	0.343 g
4.	Mass of crucible, cover, and contents after heating	27.785 g
5.	Mass of contents (mostly MgO, we hope!)	0.560 g
6.	Mass of oxygen combined with Mg	0.217 g

$$\% \text{ Mg} = (0.343\text{ g}/0.560\text{ g}) \times 100 = \mathbf{61.3\%}$$
$$\% \text{ O} = (0.217\text{ g}/0.560\text{ g}) \times 100 = \mathbf{38.8\%}$$

Theoretical values:

$$\% \text{ Mg} = (24.3/40.3) \times 100 = \mathbf{60.3\%}$$
$$\% \text{ O} = (16.0/40.3) \times 100 = \mathbf{39.7\%}$$

Here are actual results from eight student groups:

% Mg	% O
74.0	26.0
63.1	36.9
60.9	39.1
60.8	39.2
69.9	30.1
61.1	38.9
60.7	39.3
98.3	1.70 *

* This group had continual trouble with their burner. At the close of the procedure the team noted that their Mg ribbon had hardly reacted. Do not be afraid to allow "poor" data to be collected and included in group analysis. Be prepared to lead the class in discussing what could have happened.

Answers to Implications and Applications

1. This removes water vapor and oils, which can affect masses if the balance is sensitive enough.
2. This is done to admit enough O_2 and N_2 to insure that the reaction of Mg is as complete as possible.
3. Water was added to convert magnesium nitride into magnesium oxide and ammonia, thus producing a purer MgO product.

$$Mg_3N_2(s) + 3H_2O(l) \rightarrow 3MgO(s) + 2NH_3(g)$$

4. Continuing to heat and reweigh until the masses are consistent would be one way to build confidence that the reaction was as complete as possible.
5. If the mass percent of magnesium is too high, it is likely that it did not react completely or some of the magnesium had oxidized to MgO before massing. If the mass percent is too low, it is most likely because not all of the water was evaporated. There is always a possibility of error in masses. (Also see the answer to Question 8, but do not expect students to include that in their answer to this question.)
6. If the elements in the compound were known and you could determine the mass percent composition, you could probably identify the compound by comparing the percent composition to that of known compounds.

7. If the Mg is not cleaned well enough at the start, some slight error would be introduced because the initial mass of Mg would already contain MgO. (This would lead to low results, as explained in the answer to Question 5.)

*8. The final products would consist of both magnesium nitride and magnesium oxide. Upon close mathematical examination, one would conclude that the products should have a lower mass. Mg_3N_2 has a molar mass of 100.9 g/mol, and although 3 MgO's contain the same mass of Mg it would have a molar mass of 120.9 g. Failure to add water would leave the 3 Mg in the nitride, not in the 3 MgO's. It is doubtful that most high school balances could detect this mass difference (probably < 0.05 g difference).

(*NOTE: Very few students should be expected to display this much mathematical insight in answering the question.*)

* This question may be too difficult for students if stoichiometry has not been discussed at this point in the course.

Post-Laboratory Activities

1. Start by collecting class data for this activity. By posting results, a trend should emerge, revealing consistent results around 60% Mg and 40% O. Discuss how these results relate to the Law of Definite Composition.
2. Questioning about high or low percent values would be a natural follow up. Include as many students as possible in the discussion.
3. Ask such questions as "Would the amount of Mg used affect the results?" Also probe on the usefulness of knowing the percent composition of a compound. Propose that the students are chemists in charge of producing fertilizer for a company. Ask them to explain how this activity has a connection to their success in this company.

Extensions

1. A key part of this laboratory activity is to use data collected for the class (or several classes, if desired) to illustrate the importance of the mole concept and the determination of empirical formulas.
2. Ask students to calculate moles Mg and moles O from their experimental data. Plot moles Mg *vs.* moles O for the class. This usually gives a beautiful graph with the expected slope of about 1. Feel free to discard individual data points that are obviously far from the trend. These are decisions that scientists with guidance from statistics can make. Explain to students that many experimental trials are often needed to produce reliable results. With thousands of trials, data points far removed from the trend would have little effect on the overall statistical analysis of results.
3. This graph verifies the formula for magnesium oxide (MgO) that students used to calculate their theoretical mass percent values for Mg and O. Explain how the slope of the graph can be used to determine the empirical formula. (Alternately, extrapolate the graph to 1 mol Mg and show that the corresponding value for O is also 1 mol.)
4. Have students investigate common substances made up of the same elements that differ in their percent composition by mass, such as H_2O_2 and H_2O. Establish differences in their properties and uses.

5. Invite students to investigate a major industrial chemical process such as the Haber, Ostwald, Contact, or Hall process to identify major reactants and to reinforce the notion that knowledge of amounts of required substances is a component of being a successful industrial chemist or engineer.

Assessing Laboratory Learning

Laboratory Practical

Provide students with sample data on another compound composed of a metal and a nonmetal. Have them perform calculations to identify the compound by comparing their results to a list of "known" compound possibilities.

Examination Questions

1. Three metals are allowed to react as completely as possible to form their oxides. The possible oxides are Cu_2O, CuO, and ZnO. Which would have the highest percent oxygen by mass? *[CuO]*
2. If you were given 45.0 g of aluminum, what minimum mass of oxygen would you need to allow the aluminum to react completely to form Al_2O_3? *[40.0 g O_2]*

Other Laboratory Activities

1. A good activity is ask students to weigh a 1-in square of Al foil and calculate the number of such squares that must be stacked to provide 1 mol Al. A 1-in square of aluminum foil has almost exactly 10^8 Al atoms on each edge. Therefore, a 1-in cube of Al would approximate one mole (approximately 10^{24}) Al atoms.
2. *Determining the percent water in a hydrate.* This laboratory activity can also be used to illustrate the determination of percent composition. The calculations are not as clear to beginning students as the percent of an element in a compound (as in *Laboratory Activity 2*), but the results are usually good. (A typical laboratory experiment is given by Slowinski, 1985.)
3. *Determining Avogadro's number* (and molecular size) from measurements on a unimolecular layer of stearic or oleic acid. This activity provides a way to obtain an approximate value for Avogadro's number. The assumptions needed are usually beyond the grasp of beginning students. However, if you do not dwell on the assumptions, students can understand the calculations reasonably well and will obtain a value of approximately the correct order of magnitude (10^{22} to 10^{24}) for Avogadro's number. Corwin (1988) describes an experimental procedure.
4. *Determining an empirical formula from the reaction of Fe with $CuSO_4$.* This laboratory activity gives good results. A modified version of the activity is given in the *Stoichiometry* module. The data can be used to calculate the empirical formula for $CuSO_4$ (mole ratio of Cu^{2+} to SO_4^{2-}). The experimental procedure is the same.
5. *NOTE: We strongly discourage using the experimental determination of the empirical formula of a sulfide of copper, which you may find in older laboratory manuals.* Many individuals are extremely sensitive to the SO_2 formed in the activity. Persons with asthma can have severe reactions to SO_2.

DEMONSTRATIONS

Demonstration 1: A Molar Display

Purpose

To illustrate that one-mole samples of different substances have different volumes and masses.

Materials

One mole of various substances such as:

Water, H_2O, 18.0 g (18.0 mL)
Methanol, CH_3OH, 32.0 g (40.4 mL)
Copper (use copper dust), Cu, 63.6 g
Sodium chloride (table salt), NaCl, 58.5 g
Carbon (activated charcoal), C, 12.0 g
Sulfur, S, 32.1 g
Iron (iron filings), Fe, 55.8 g
Sucrose (table sugar), $C_{12}H_{22}O_{11}$, 342 g

Safety

No special precautions are needed if the above-listed substances are used.

Procedure

Display one mole of several different substances in identical containers, pointing out that one-mole samples of different substances have different volumes. Weigh one mole of several different substances to illustrate that moles of different substances have different masses. Suggestions of substances to use: water, methanol (or other alcohol), sucrose, salt, carbon, sulfur, iron filings, copper dust or other solids that are finely divided so the observed volume approximates the volume of the solid.

Demonstration 2: Molar Measurements

Purpose

To illustrate that the mole is a unit of measurement. (Extension of above demonstration.) This would also be an appropriate follow-up demonstration to the *Understanding the Mole* activity.

Materials

One mole and multiples and submultiples of a mole of a particular substance. For sodium chloride (table salt), NaCl, possible quantities are:

NaCl (0.100 mol), 5.85 g
NaCl (0.500 mol), 29.2 g
NaCl (1.00 mol), 58.5 g
NaCl (2.00 mol), 117 g
NaCl (5.00 mol), 292 g
NaCl (10.0 mol), 585 g

Safety

No special precautions are required if NaCl is used.

Procedure

Weigh one mole of a substance—for example sodium chloride or granular metal (Fe, Zn, *etc.*)—and arrange in a pile or heap. Label the pile "one mole NaCl" (or "one mole Zn," *etc.*) Prepare several other piles of the same substance to represent different numbers of moles (1/2, 2, 3, 5, *etc.*); ask students to guess the number of moles of substance in each pile. Use this demonstration to discuss the concept that the mole is a way to measure substances—if one knows the amount that one mole represents, one can determine how many moles are present in quantities larger or smaller than one mole. (You could use sugar or salt packets and have students empty the contents and guess the number of moles. They could then weigh the substance and calculate the number of moles to check their answer. If desired, students could also calculate molecules of sugar, grams of carbon present, *etc.*)

Since "mole" means "pile" or "heap" and molecule means "smallest part of the pile or heap," you could also use this demonstration to highlight the difference between the terms "mole" and "molecule." Of course, students cannot see a molecule (or atom) of the substance, but if you use a granular substance, they can see that there are many "grains" in a pile and must therefore be many more molecules in a pile.

Demonstration 3: How High the Mole

Purpose

To help students visualize the size of Avogadro's number.

Materials

Mole Demo, a Seraphim computer program (see reference to AP 305, AR 301, PC 2301 in *Media* section)

Safety

No safety precautions are necessary

Procedure

The *Mole Demo* computer program illustrates the stacking of sheets of paper from earth to Pluto. Use this after introducing the mole and Avogadro's number to help students realize the magnitude of Avogadro's number.

Remarks

This program requires about 5 min. Since there is no dialog (but musical sound effects occur periodically), consider preparing your own running commentary to accompany the program.

Demonstration 4: Moles and Gases

This demonstration is on the Ring of Truth: Atoms *videotape and is also illustrated on CHEM Study video Gases and How They Combine (see references in* Media *section).*

Purpose

To illustrate the relation between gas volume and moles of gas.

Materials

Electrolysis apparatus (an inexpensive electrolysis apparatus is available from scientific supply vendors)
Distilled water
0.1 M Sulfuric acid, H_2SO_4, several milliliters (to serve as electrolyte to facilitate electrolysis)
Wooden splint (and match to ignite splint)

Safety

Observe usual safety precautions in handling the sulfuric acid. Follow directions supplied with electrolysis apparatus to set up the demonstration. Although the danger is slight for the small quantity of hydrogen produced in the electrolysis demonstration, the hydrogen could explode if ignited.

Procedure

An understanding of stoichiometry (or at least the meaning of formulas) is needed for students to understand this demonstration. Since the electrolysis of water produces two moles of hydrogen gas for every mole of oxygen gas, the volume of hydrogen formed in the electrolysis is twice the volume of oxygen. Consult directions accompanying the electrolysis apparatus to conduct the electrolysis demonstration. Collect 25-50 mL of the gases during electrolysis, or enough for the class to see that the volume of one gas is approximately twice the volume of the other. The gases collected can be tested to verify which is oxygen.

Ask the class to decide which gas is oxygen on the basis of the stoichiometry for the reaction (or the formula for water). Test only that gas. (Insert a glowing splint into a sample of the gas. If the splint bursts into flame, the gas is oxygen.) Warning: Do not attempt to ignite hydrogen as a proof that the other gas is hydrogen. Students will accept that the other electrolysis product must be hydrogen if water is electrolyzed.

GROUP AND DISCUSSION ACTIVITIES

1. Ask students to construct (from poster board) a 22.4 L cube so they can visualize the volume of one mole of gas at STP. (A typical 5 gal waste paper basket contains about 20 L, also a good approximation for the molar volume of a gas.)
2. Challenge students to calculate the number of molecules (formula units) present in various volumes of water or amounts of other substances (*i.e.*, molecules/moles in a grain of salt or sugar, drop of water, sugar cube, sugar or salt packet, *etc.*)
3. Students could set up *Demonstration 2* (each group using a different substance), organized as a game in which other students guess the number of moles.

Key Questions

1. Why do chemists often refer to moles of a substance rather than molecules (or atoms or formula units)? *[The mole is a convenient size unit to express the amounts of substances involved in laboratory-scale reactions.]*
2. How are moles, mass, and number of entities for a sample of matter related? *[1 mol of entities = formula mass (in grams) x (the molar mass) = 6.02×10^{23} entities]*
3. What is the relationship of moles to volume of a gas at STP? *[For an ideal gas at STP, 1 mol = 22.4 L]*
4. How is percent composition related to mole ratios? *[The percent of an element (A) in a compound is given by:*

$$\%A = \frac{\textit{(moles A in compound) x (molar mass A)}}{\textit{(1 mol compound) x (molar mass compound)}} \times 100$$

5. How is the empirical formula related to the mole ratios of elements in a compound? *[The empirical formula relates to the relative numbers of moles of each element in the compound. The relative numbers of moles expressed as integers are the subscripts in the empirical formula. For example, if a compound contains 1.5 mol A for every mole of B, the ratio expressed as integers is 3:2—the empirical formula for the compound is A_3B_2.]*
6. Explain why equal masses of different substances do not contain equal numbers of molecules or moles. *[Since different substances usually do not have the same molar mass, one mole or Avogadro's number of entities (molecules, etc.) will have different masses. Therefore, equal masses must contain different numbers of moles or molecules.]*

Counterintuitive Example

1. 200 g of lead has fewer atoms than 1 g of hydrogen. (Other examples can be given.) One mole of lead (208 g) has the same number of atoms (Avogadro's number, or 6.02×10^{23}) as one mole of hydrogen (1 g). However, 200 g of lead is less than one mole of lead and has fewer than Avogadro's number of atoms, thus fewer than 1 g of hydrogen.

Analogies

1. A mole (6.02×10^{23}) is a counting number like dozen (12), gross (144), ream (500), *etc.* used to count objects such as eggs, pencils, or sheets of paper. Because atoms are so very small, measurements using ordinary laboratory-measuring equipment can only be made on very large numbers of them—on the order of Avogadro's number.
2. Astronomers estimate that there is a mole (6.02×10^{23}) of stars in the universe.
3. Analogy to mole/mass/molecule calculations: Counting rolls of coins and determining the number of coins and their value is analogous to mole/mass/molecule calculations, as the following activity suggests.
4. **Roll-Mole Analogy** (by Caroline L. Ayers). As anyone who has taught chemistry knows, the mole concept is one of the most difficult in chemistry. The roll analogy was devised to show students that calculations involving moles are similar to some they can easily do—calculations involving money. Any student can do relatively complex calculations if they involve money.

   The Roll-Mole Worksheet (which follows) is designed to be used by answering Problems 1, 2, 1', and 2' first. Then have students fill in the blanks on the equalities. After this point, students are told to "forget" that a nickel is worth 5¢ and a quarter is worth 25¢. They must not use that information in solving Problems 3 through 6 or the purpose of the exercise is defeated. (Nobody remembers the mass of an atom of an element or a formula unit of a compound!) The worksheet points out the information students are allowed to use to solve the problems. To use the worksheet most effectively, work Problem 3 and 3' side-by-side on the board so students see that the reasoning is identical.
   Students should be made aware of the reasoning (use a set up) for each

$$3 \text{ rolls nickels} \times \frac{40 \text{ nickels}}{1 \text{ roll nickels}} = 120 \text{ nickels}$$

$$3.00 \text{ mol S} \times \frac{6.02 \times 10^{23} \text{ atoms S}}{1 \text{ mol S}} = 1.81 \times 10^{24} \text{ atoms S}$$

   problem so that they will recognize that moles are not really impossible to work with—Avogadro's number is just too large to picture. Students resist setting up the money problem. They say they do not know how they do it, they just do it. That is because such calculations are so familiar and thus easy to do. If they cannot tell what the set up should be, tell them and write it down, including units so they can see the units cancel out just as in the corresponding mole problem. Work Problems 4 and 4' together, *etc.* In the analogy, value (\$) is like mass (g), number of coins is like number of atoms, and rolls of coins are like moles of atoms. (Note that "roll" rhymes with "mole".)

Roll-Mole Analogy

Given the following information: There are 40 nickels in a roll.
There are 40 quarters in a roll.

Answer these questions. Show Set Up!

(1) What is the value of a roll of nickels?

(2) What is the value of a roll of quarters?

(1') What is the mass of a mole of S?

(2') What is the mass of a mole of Br?

_____ nickels = 1 roll nickels = $_______

_____ quarters = 1 roll quarters = $_______

______________ atoms S = 1 mole S = ________ g S

______________ atoms Br = 1 mole Br = ________ g Br

Use only the above equalities to answer the following questions:

(3) How many nickels are in 3 rolls of nickels?

(4) What is the value of 3 rolls of nickels?

(5) How many rolls of quarters is $500?

(6) How many nickels are in $500 of nickels?

(3') How many atoms of S are in 3.00 mol S?

(4') What is the mass of 3.00 mol S?

(5') How many moles are in 53.8 g Br?

(6') How many atoms are in 1.5 g Br?

Answers: (1) $2 (2) $10 (3) 120 (4) $6 (5) 50 (6) 10,000 (1') 32.1 g S (2') 79.9 g Br (3') 1.81×10^{24} atoms S (4') 96.3 g S (5') 0.673 mol Br (6') 1.1×102^{2} atom Br

4. *Empirical Formula Analogy* (by Kerro Knox, 1980)

   Given the average mass (weight) of boys and girls in a class and the percent boys by mass and percent girls by mass, calculate the ratio of boys to girls and the "formula" for the class (B_xG_y).

Example:	Average mass of boys	72 kg (160 lb.)
	Average mass of girls	54 kg (120 lb.)
	Percent boys in class	66.6%
	Percent girls in class	33.3%

   Assume 100 kg of the class. The class would be 66.7% x 100 kg = 66.7 kg boy (B) and 33.3% x 100 kg = 33 kg girl (G).

$$66.7 \text{ kg B} \times \frac{1\text{B}}{72 \text{ kg B}} = 0.93 \text{ B}$$

$$33.3 \text{ kg G} \times \frac{1 \text{ G}}{54 \text{ kg G}} = 0.62 \text{ G}$$

$$\frac{0.93 \text{ B}}{0.62 \text{ G}} = \frac{1.5 \text{ B}}{1.0 \text{ G}} \times \frac{2}{2} = \frac{3.0 \text{ B}}{2.0 \text{ G}}$$

   Formula for the class = B_3G_2

5. Analogies to illustrate the size of Avogadro's number

   a. One mole of high school textbooks would cover the USA to a depth of about 320 km (200 miles).

   b. Water flows over Niagara Falls at about 650,000 kL (172,500,000 gallons) per minute. At this rate it would take 134,000 years for one mole of water drops (6.02×10^{23} drops) to flow over Niagara Falls.

   c. Avogadro's number (6.02×10^{23}) is the approximate number of milliliters of water in the Pacific Ocean (7×10^8 km^3 or 7×10^{23} mL). (Analogy by M. Dale Alexander, Gordon J. Ewing, and Floyd T. Abbott, 1984.)

   d. If one mole of particles the size of sand grains were released by the eruption of Mount St. Helens, they would cover the entire state of Washington to the depth of a ten-story building. (Analogy attributed to Glenn Crosby.)

   e. Analogies by A. Truman Schwartz and Lucy T. Pryde:

      One mole of marshmallows would cover the USA to a depth of 105,000 km (6500 miles). *NOTE: The volume of a marshmallow is estimated as 16 cm^3 (1.0 in^3). The area of the USA is 9.32×10^6 km^2 or 3.6×10^6 mi^2.*

      If an Avogadro number of pennies were distributed evenly among the 4.9×10^9 human inhabitants of earth, each man, woman, and child would have enough money to spend a million dollars every hour—day and night—and still have over half of it unspent at death.

      One guacamole is the amount of taco chip dip that can be made from an Avogadro number of avocados—plus appropriate quantities of tomatoes, onions, and chili. A train stretching to the North Star and back 2-1/2 times would be required to transport one guacamole. *NOTE: This assumes that the volume of one standard avocado (pit removed) is 278 cm^3 and that other ingredients make up 25% of total volume. The average coal car has a capacity of 110 kL (4000 ft^3) and is 16 m (53 ft) long. The North Star is 680 light years distant.*

Suppose the Greek god Zeus, after observing the Big Bang 15 billion years ago, became bored and decided to count one mole of atoms. Zeus is omnipotent. He can count very fast (one million atoms per second) and, of course, never sleeps. He has currently completed over three-fourths of the task, and will be finished in just another four billion years.

One mole of moles (animal-type), placed head to tail, would stretch 11 million light years and weigh 9/10 as much as the moon. *NOTE: Each mole is assumed to be 17 cm long with a mass of 100 g. Speed of light = 3.0×10^8 m/s. Mass of moon = 6.7×10^{22} kg.*

One mole of marbles, each 2 cm in diameter, would form a mountain 116 times higher than Mount Everest. The base of the marble mountain would be slightly larger than the area of the USA. *NOTE: Marbles are assumed to have hexagonal closest packing and the mountain has a cone of angle 30°. Area of USA = 9.32×10^6 km^2. Volume of cone = $\pi r^2 h/3$, h = height = $r \tan 30°$.*

TIPS FOR THE TEACHER

Language of Chemistry

1. The term "formula unit" is used in this module to refer to the smallest unit of a substance of a defined formula. For example, one formula unit of CO_3^{2-} refers to one CO_3^{2-} ion. One formula unit of Ne would be one Ne atom. This terminology is especially useful when referring to ionic compounds because "molecules" of solid ionic compounds do not exist. One formula unit of NaCl, consists of one Na^+ ion and one Cl^- ion. Likewise, a formula unit of $CuSO_4 \cdot 5H_2O$ contains one Cu^{2+} ion, one SO_4^{2-} ion, and 5 H_2O molecules. Because the molar mass of any substance is defined on the basis of its formula, the use of the term "formula unit" is not necessary. It is used here to avoid referring to atoms, molecules, ions, *etc.* each time we refer to moles.
2. Due to the SI definition of mole, there is no official basis for using the terms "gram moles," "pound moles," "ton moles," *etc.* even though these are sometimes still encountered. The molar mass is the mass of one mole of any species expressed in grams.
3. "Formula weight," "gram formula weight," "molecular weight," "gram molecular weight," and "atomic weight" are terms that refer to moles of specific categories of substances. These are used synonymously with "molar mass," which remains the preferred term.
4. The meaning of formulas in terms of moles (rather than atoms) should be stressed so students begin to think "moles" rather than "atoms," "molecules" or "formula units" when they see a formula or interpret its meaning. This will greatly facilitate calculations encountered later in this module (percent composition and empirical formula) and stoichiometry problems, which follow soon after this topic in most texts.
5. The empirical formula is the simplest formula for a substance. In the empirical formula the subscripts are reduced to the smallest possible integers. The formulas for many ionic substances are empirical formulas; however, molecules of covalent substances are frequently a multiple of the empirical formula. The formula for a molecule is called the molecular formula. The empirical formula for a covalent compound is found by dividing all the subscripts by the largest common factor (*e.g.*, the empirical formula for $C_6H_{12}O_6$ is CH_2O).

Common Student Misconceptions

1. **"Equal volumes or equal masses of different substances contain the same number of moles (or atoms/molecules/formula units)."**

   It *is* true that equal volumes of gases contain the same number of moles of gas molecules (assuming equal temperatures and pressures), but such an assertion is wide of the mark for liquids or solids. No such generalizations are possible for the masses of substances—whether in gaseous state or not.

2. **"The term 'mole' refers only to 'molecules.' "**

   This is particularly problematic if the mole concept is only applied to molecules (or formula units). It is advisable to apply the concept of moles also to ions, electrons, and/or other entities so that students will not associate "mole" exclusively with the term "molecule."

3. **"One mole of various substances may contain different numbers of units of those substances."**

   Although Avogadro's number (6.02×10^{23}) is such a large number that it cannot be meaningfully visualized, it is important that students conceive of one mole of a substance as containing the *same number of units* as one mole of any other substance. However, you must work hard to destroy the idea that equal masses or equal volumes of two substances contain the same number of moles, as was highlighted in Misconception 1.

Problem Solving

1. Problem solving is essential to understanding the mole concept. It is important to illustrate a variety of permutations (moles to grams, volume of gas at STP to mass, molecules to moles, *etc.*) when solving mole problems. Practice should be given, initially with your assistance and later as independent assignments. After students master mole-mass and mass-mole conversions, proceed to percent composition problems. When percent composition problems are understood, the concept of empirical *vs.* molecular formula can be introduced and empirical formula problems can be solved. The determination of molecular formulas from empirical formulas and molar masses can be introduced either before or after problems dealing with calculating empirical formula.

2. In demonstrating how to solve mole-mass-entity problems, emphasize the relationship of mass and number of entities (molecules/atoms/formula units/ions, *etc.*) to moles. Suggest that students devise an equality that relates mole/ mass/molecules for the substance in the question. For example:

   $$1 \text{ mol HCl} = 36.5 \text{ g HCl} = 6.02 \times 10^{23} \text{ molecules HCl}$$

   The mass (grams) of the substance can be converted to moles by using this relationship to construct a "unit conversion factor" and the unit-label method. Since *mole* is the unifying idea, if the number of molecules is desired and mass is given, mass should be converted to moles and then moles to molecules, using two factors (see transparency master).

   Example: How many molecules are in 146 g HCl?

$$146 \text{ g} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \times \frac{6.02 \times 10^{23} \text{ molecules HCl}}{1 \text{ mol HCl}} = 2.41 \times 10^{24} \text{ molecules HCl}$$

3. If you prefer an algebraic approach, a generalized form of the relationship among mass, moles, and entities is:

$$\frac{\text{g X}}{\text{molar mass X}} = \text{mol X} = \frac{\text{number of X's}}{N_A}$$

$$\text{X = formula;} \quad N_A = \text{Avogadro's number}$$

4. In percent composition problems, it is useful to illustrate the calculation using a compound having more than one atom of some element (*e.g.*, K_2O) to illustrate that the total mass (2 x molar mass K atoms, not molar mass of K atoms) is used to calculate percent composition. It is a very common error to use the mass of 1 mol K (rather than 2 mol K) in calculating the percent K in K_2O. The resulting mass percent potassium will be incorrect (too low by a factor of two). Remind students that the sum of the percents should be 100 (or close to 100).
5. One procedure for solving percent composition problems can be outlined using the mole concept:

$$\frac{\text{Total moles of element x Formula mass of element}}{\text{1 mol compound x Formula mass compound}} \text{ x } 100 = \text{\% of element in compound}$$

6. When illustrating empirical formula problems, start with a binary compound containing subscripts that are simple multiples of each other (*e.g.*, CO_2, PCl_3, CH_4). Then proceed to a binary compound where the mole relationship is more complex (2 to 3 or 3 to 4), requiring the additional step of multiplying by an integer to convert relative numbers of moles to integers. In solving empirical formula problems emphasize that subscripts give the relative numbers of moles of elements in the compound; if we know the relationship of the moles of the elements we know the subscripts. This type of problem is difficult for most students. Provide needed practice, both supervised and independent.
7. If students set up empirical formula problems "upside down" (*i.e.*, divide atomic mass by mass of the element rather than calculate moles correctly), their subscripts will be opposite to what they should be (*i.e.*, they will get the correct subscripts but for the wrong elements). Watch for this and reemphasize that students calculate moles of the elements. Of course, the units will be incorrect if students set up the problem this way, but that does not seem to bother many students. This would be a good place to emphasize how to use units to check that the problem solution is reasonable.

   The procedure for solving empirical formula problems can be outlined using the mole concept:

   $$\text{[Percent composition]} \rightarrow \text{Masses of elements} \rightarrow$$
   $$\text{Ratio of moles of elements} \rightarrow \text{Empirical formula for compound}$$

HISTORY: ON THE HUMAN SIDE

1. The mole concept is attributed to Amedeo Avogadro, who postulated that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. He based this hypothesis on Gay-Lussac's Law of Combining Volumes (when two gases react, their volumes are in whole number ratios) and Dalton's Atomic Theory (substances combine in integral ratios of atoms). Avogadro proposed that gases exist as molecules that can be composed of more than one atom of an element and that these molecules can break up during reaction. Avogadro, however, never determined what we know today as Avogadro's number.

2. Because Dalton and other influential scientists of his day did not accept his hypothesis, Avogadro's idea was not accepted for many years. After his death, Avogadro's hypothesis was "rediscovered" and accepted. When the number of molecules in a mole was estimated by Perrin during the early years of this century, he suggested that the number be called Avogadro's number. Since that time, Avogadro's number has been measured by several different methods, including a measurement by Rutherford using alpha particles and the measurement by Millikan in his famous oil-drop experiment in which he determined the charge on an electron. More recently, Avogadro's number has been measured by X-ray crystallographic measurements.

HUMOR: ON THE FUN SIDE

1. A poem by Doris Kolb (from *J. Chem. Educ., 1978*):

A mole is a particular amount
Of a substance–just its formulary weight
Expressed in grams, with Avogadro's count
Of units making up the aggregate.
A mole is a specific quantity:
Its volume measures twenty-two point four
In liters (for a gas at STP).
A mole's a counting unit, nothing more.
A mole is but a single molecule
By Avogadro's number multiplied;
One entity, extremely miniscule,
A trillion trillion times intensified.
A mole is an expedient amount,
For molecules are just too small to count.

2. Mole Song (to "Deck the Halls")

Avogadro's Number makes one
mole of atoms or of molecules.
Changing it to grams is easy
If you know what things to use.
Multiply it by a fraction
Molar mass over one mole.
Then you calculate your answer
Canceling like terms, you'll reach your goal.

3. A mole stuffed animal can be obtained from American Bear, Inc., 401 N. Wabash, Suite 500, Chicago, IL 60611 (The Hole in the Ground Gang Mole #1407. Phone number: 312-329-0020.)
4. Mole posters and shirts available from Mole Reproduction, 315 Lincoln Street, Verona, WI 53593.
5. Classified ad:

FOR MOLE CONTROL
CALL
∞ 602 – 1023 ∞
A. Avogadro

6. A one-molar solution:

7. Message on a T-shirt: A Chemist is a Mole's Best Friend.
8. Sign on a bumper sticker: Everyone has...Avogadro's Number—6.023×10^{23}.
9. **THE MOLE**

You say a mole is brown and furry
with eyes developed wrong,
You ask a chemist his description
which is quite a different song.
A chemists mole is not of fur,
nor is it very brown,
It comes in many varieties—square, oblong,
or round.

The mole can stand for numbers, formulas
or items of everyday,
A mole of girls, a mole of boys, whatever
you wish to say.
Chemists indulge jubilantly,
solving problems it creates,
My brains find problems no fun at all
pondering them till it aches.

CHEM 13 NEWS, February 1972, p. 393

10. The Mole Joke Book (CHEM 13 NEWS, February 1983, p. 12 and October 1983, p. 3):

QUESTIONS

1. What did Avogadro give his ex-wife every month?
2. What did Avogadro have on his pancakes?
3. On which American mountain was Avogadro's face carved in stone?
4. What song did Avogadro's family sing on New Year's Eve?
5. Where did Avogadro send his CARE packages?
6. Why was there only one Avogadro?
7. What was Avogadro's favorite board game?
8. What kept Avogadro in bed for two months?
9. Who was Avogadro's favorite singing group?
10. Who was Avogadro's favorite composer?
11. Avogadro loved to watch M.A.S.H. Which character did he like the most?
12. What did Avogadro call his church services?
13. How would you have described Avogadro's room while he was a teenager?
14. Which was Avogadro's favorite Indian tribe?
15. Which recent movie would Avogadro have really liked?
16. What did Avogadro think of hemorrhoids?
17. What did Avogadro put into the pockets of his tweed suit?
18. Can you name two movies that Avogadro really liked?
19. What was Avogadro's best day in golf?
20. How did Avogadro send a secret message with his walkie-talkie?

21. What is Avogadro's favorite kind of music?
22. Which Walt Disney characters was Avogadro fond of?
23. What is Avogadro teaching his astronomy class about?
24. What do you get when you have a bunch of moles acting like idiots?
25. How did Avogadro help his team win the soccer playoffs?
26. Which is one of Avogadro's best songs?
27. What did Avogadro invent for his wife to use as a night cream?
28. What was Avogadro's favorite drink?
29. Why did people say Avogadro was lazy?
30. What is Avogadro's favorite chocolate bar?
31. What did Avogadro get when he mixed ice cream, chocolate syrup, and milk?
32. What kind of shell-fish did Avogadro like to eat?
33. Which tooth did Avogadro have pulled out?
34. What religion did Avogadro belong to?
35. What did Avogadro's bird do when it was time for him to send his feathers?
36. What was the mad bomber's favorite drink?
37. Where did Mrs. Avogadro do her shopping?
38. What did Avogadro teach his students in math class?
39. What are moles made of?
40. Which team lost the World Series in 1982?
41. What brand of cigarettes did Avogadro smoke?
42. What are mammoles?
43. What do you sue to flatten hot asphalt?
44. How did Avogadro get through the desert?
45. What do chemists do in a math class?
46. Which part of the universe did Avogadro like to study?
47. What kind of fruit did Avogadro eat in the summer?
48. How much money did Avogadro make from being a chemist?
49. What is Avogadro's favorite sport?
50. What is Avogadro's favorite drink?
51. What happened to Avogadro when he had to drive over a bridge?
52. What area did Avogadro explore?
53. What were Avogadro's houses made of?
54. How much does Avogadro exaggerate?
55. What did J. J. Thomson have for dessert?
56. What happens to Avogadro's dog in the summer?
57. What did Avogadro do when he lost his job?
58. Where does Avogadro plant his trees?
59. What was Avogadro's best subject?
60. What was Avogadro dressed as when he went to the masquerade ball?
61. Where did Avogadro go sailing?
62. What was the problem Avogadro had with his shoes?
63. At what time was Avogadro at his romantic best?
64. What are Avogadro's favorite places?
65. What scientist was a member of the pig family?
66. What is Avogadro's favorite character?
67. What was Avogadro full of?
68. What is Avogadro's favorite song?
69. What did Avogadro collect at the seashore?
70. Where do students graduate?

ANSWERS to the Mole Joke Book

1. Alimoley
2. Moleasses
3. Mount Rushmole
4. "Mole Lang Syne"
5. Moleasia
6. When they made him, they broke the moled.
7. Moleopoly
8. Moleonucleosis
9. The Moleing Stones
10. Molezart
11. Father Molecahy
12. Molar mass
13. A Molar mess
14. The Molehawks
15. "On Moleton Pond"
16. They're a pain in the mass.
17. Molth balls
18. "Mole Miner's Daughter" and "Moleby Dick"
19. When he got a mole-in-one.
20. He used the Molse Code.
21. Rock + Mole
22. Mickey and Minnie Mole
23. The molar system
24. A bunch of moleasses.
25. He scored the winning mole.
26. "There's a mole in my bucket, dear Liza, dear Liza..."
27. Oil of Molay
28. Moleson Export Ale
29. They said he was as slow as moleasses.
30. Molted milk
31. A chocolate molted
32. Mole-uscs
33. One of his molars
34. Molslem
35. It moleted
36. Moletov cocktails
37. In a shopping mole
38. Moletiplication
39. Molecules
40. The Molewaukee brewers
41. DuMolier
42. Four-legged animoles
43. A steam-moler
44. On a camole
45. Moletiply
46. The Moleky Way
47. Watermolens
48. Enough to make him into a moleionnaire.
49. Lawn moles
50. Coca molar
51. He had to pay at the mole gate.
52. The South Mole
53. Moleskin
54. He makes mountains out of mole hills.
55. Plum pudding
56. It molets.
57. He joined the mole queue.
58. Moles in the ground.
59. Mass
60. An avocado
61. The Moleucca Strait
62. He wore the mole out too quickly.
63. On Mole-lit nights
64. Moland, Massachusetts
65. Niels Bohr
66. Masswell Smart
67. Molar energy or 6 x 10^{23} particles
68. Molar Kintyre
69. Mole-uscs
70. At moleage

11. In the U.S., Mole Day is celebrated on Oct. 23 (10/23) from 6:02 a.m. to 6:02 p.m. In Europe, Mole Day is celebrated on Feb. 6 (6/02) from 10:23 a.m. to 10:23 p.m. (In the U.S., dates are written month/date; in Europe, date/month.)

12. Word Search (see *Appendix* for master copy)

~~A V O G A D R O S N U M B E R~~ O T
G T F V C M C L S S D S A Y K K S
I V I O B D D X S M R L J J V X T
A V I O W S Y V A R U H U E N E N
O U M D S V N O M M W B D F W J E
Y ~~G R A M~~ O H W R J U T S A M B I
S Q W O B X X O A V X T D A G O C
T V N R R T F T L Z B P F D G L I
E D A ~~Y R T E M O I H C I O T S~~ F
D C F Z B G T I M S N W X Y R D F
M C ~~M O L E C U L E S~~ A X A L P E
S T W X T I Z Y L U ~~E L O M~~ J K O
D X R I I O O C D R S F W U G K C

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. A ____ of a substance represents Avogadro's number of units of that substance.
2. 6.02 x 10^{23} (2 words).
3. Mass, in grams, of 1 mole of a substance (2 words).
4. SI unit of mass ÷ 1000
5. __________ describes the quantitative relationships among elements and compounds as they undergo chemical changes.
6. Symbolism showing a substance's chemical composition.
7. Smallest units of compounds.
8. Numerical multipliers showing ratios between reactants and products in a chemical equation.
9. One mole of a substance in this state at STP occupies a volume of 22.4 L.
10. One mole of this element weighs 12.0 g.

Answers: 1. MOLE 2. AVOGADRO'S NUMBER 3. MOLAR MASS 4. GRAM 5. STOICHIOMETRY 6. FORMULA 7. MOLECULES 8. COEFFICIENTS 9. GAS 10. CARBON

13. See cartoons at end of module.

MEDIA

1. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

   a. For the Apple II computer running on ProDOS: AR 301, AR 302, AR 305

   b. For the Apple II computer: AP 304, AP 305, AP 306, AP 307

   c. For IBM PCs and PC-compatibles: PC 2201, PC 2301

2. "The Atom" videotape from the *Ring of Truth* series by Philip Morrison includes about a 3-min segment on the mole idea (reaction of different volume ratios of gases). Videotapes are available through PBS (800-424-7963). (To appreciate the entire tape, students probably need a broader understanding of chemistry than is held by the average student at the point in which development of the mole concept generally occurs in the high school chemistry course.) Essentially the entire text of the tape and all important visual images are also included in the book *The Ring of Truth: An Inquiry Into How We Know What We Know* by Philip and Phyllis Morrison (1987). PBS address (Ring of Truth):

   PBS Video
   1320 Braddock Place
   Alexandria, VA 22314
   (703) 739-5000

3. The video *Powers of Ten* goes from galaxy size down to nuclear size. It may help students visualize the size of atoms and the comparison of Avogadro's number in terms of powers of ten (Morrison, 1982). Video available from Video Catalog, P.O. Box 64428, St. Paul, MN 55164-0428 or High Bridge Co., 1000 Westgate Drive, St. Paul, MN 55114-1631.

4. CHEM Study Video: Vol. 12, *Gases and How They Combine.* (1989). Illustrates Avogadro's Hypothesis (equal volumes of gases contain equal numbers of molecules). Available from Ward's Natural Science Establishment, Inc., P.O. Box 92912, Rochester, NY 14692-9978.

5. Videodiscs published by *JCE:* Software, a publication of the *Journal of Chemical Education,* Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   "A Generic Spectroscopic Instrument" and "The Mole – From Counting to Weighing," two chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc I (double sided, 60 min.), Special Issue 3.

6. The *World of Chemistry* videotape "Number 2: The Mole." World of Chemistry Videocassettes. Annenberg/CPB Project, P.O. Box 1922, Santa Barbara, CA 93116-1922; (800) 532-7637; World of Chemistry Series, Atlantic Video, 150 South Gordon Street, Alexandria, VA 22304; (703) 823-2800 or QUEUE Educational Video, 338 Commerce Drive, Fairfield, CT 06430; (800) 232-2224.

EQUIPMENT AND INSTRUMENTATION

A simple electrolysis apparatus suitable for the electrolysis of water to illustrate the relation of the mole to gas volume is available from laboratory equipment vendors.

Links/Connections

WITHIN CHEMISTRY

1. Since the mole is the central concept in quantitative chemistry, it is related to almost all topics supported in high school chemistry. Here are some examples:

   a. **Chemical Reactions and Stoichiometry**. The law of conservation of mass requires that the same numbers of atoms of all species be present before and after reaction. Because the small size of atoms makes it impractical to count atoms, chemists use moles of atoms. In balancing chemical equations, the coefficients are related to the moles of substances present. The relationship of moles of reactants and products in balanced equations is central in determining mass relationships in chemical reactions (stoichiometry).

   b. **Solutions**. Chemists generally express solution concentration in terms of molarity (moles of solute per liter of solution) or mole fraction (moles of solute per total moles in solution). Because chemical reactions are based on moles, molarity is convenient in determining the quantities of solutions needed for chemical reactions. Colligative properties of solutions (freezing point depression, boiling point elevation, osmotic pressure, vapor pressure lowering) are related to the moles of solute particles in solution.

   c. **Rates of Reaction**. Rates of reaction are often expressed in terms of moles of reactant per liter (mol/L) disappearing per unit time (or some quantity related to molarity, such as pressure of gas, absorbance/transmittance of light, *etc.*).

   d. **Equilibrium**. Since coefficients in a balanced equation relate moles of reactants and products, quantities of substances present at equilibrium are usually expressed in terms of molarity (moles/liter) for reactions in solution or pressure (which is proportional to moles per liter) for gases.

   e. **Acids and Bases**. A monoprotic acid is a compound that can furnish one mole of hydrogen (hydronium) ions per mole of compound. A diprotic acid can furnish two moles of hydrogen ions per mole of compound; a triprotic acid three. When soluble acids and bases react, the net ionic equation involves one mole of hydrogen (hydronium) ion and one mole of hydroxide ion. The pH of a solution is related to the molarity (moles/liter) of hydrogen (hydronium) ion present in solution.

   f. **Electrochemistry and Oxidation-Reduction**. In oxidation-reduction reactions, transfer of electrons accompanies chemical change. Electrochemical reactions can be described by indicating the number of moles of electrons (Faradays) transferred per mole of reactant species oxidized or reduced. In electrolysis reactions, current, time, and amount of product are related to the moles of electrons involved.

   g. **Gases**. The amount (moles) of a gas sample as well as its temperature and pressure determine its volume. (The ideal gas law relates these four quantities.) Since the volume of a gas at constant temperature and pressure is proportional to the amount of gaseous substance, the relative volumes of reactant and product gases provide a convenient method for determining or monitoring the stoichiometry of gaseous reactions.

h. **Thermochemistry**. In a thermochemical equation, the physical states of all reactants and products as well as the mole relationships among reactants and products determine the quantity of energy involved. The thermal energy involved in a reaction is proportional to the amounts (moles) of reactants used and products formed.

i. **Condensed States**. The molar heat of fusion (thermal energy required to melt one mole of substance), the molar heat of vaporization (thermal energy required to evaporate one mole of substance), and the molar heat capacity (thermal energy required to raise the temperature of one mole of substance by one degree) are all commonly used quantities.

2. When chemists prepare new compounds (particularly organic compounds), one way the compound can be characterized is from the elemental analysis. A sample of the compound is sent to a laboratory that provides the mass percent of each element (*e.g.*, % C, % H, % O, % N, *etc.*). From this information, the chemist can derive the empirical formula for the compound. Generally, spectral data (infrared, ultraviolet, nuclear magnetic resonance, mass spectrum, *etc.*) are used to predict the structure and to deduce the arrangement of the atoms in the molecule. From spectral data and knowledge of chemistry (prediction of the reaction products based on analogous reactions with known products), the chemist proposes a formula and structure for the compound. If the empirical formula of the proposed compound and the empirical formula predicted from elemental analysis agree, the proposed structure is possible. If they do not agree, the proposed structure is incorrect and additional studies must be made to identify the compound.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

Since the mole is central to chemistry, related areas such as medicine, biochemistry, biology, geology, physics, agronomy, and environmental science use the mole concept with reference to chemical processes important in those disciplines. A few examples are given below.

1. The mole (particularly millimoles and molarity) is a commonly used unit in medicine. For example, concentrations of intravenous solutions and drugs are expressed in terms of moles.

2. For the complete oxidation of glucose using the glycolytic pathway and the Krebs cycle, 38 moles of ATP are produced per mole of glucose metabolized.

$$C_6H_{12}O_6 + 36ADP + 36H_3PO_4 + 6O_2 \rightarrow 6CO_2 + 42H_2O + 38ATP$$

The amount of ATP formed in a biochemical reaction is related to the energy since the hydrolysis of each mole of ATP corresponds to 31 kJ of free energy. For the metabolism of glucose in the Krebs cycle, energy production efficiency is roughly 40% (approximately 1.2×10^3 kJ/mol glucose in the Krebs cycle compared to approximately 2.9×10^3 kJ/mol glucose for combustion of glucose to CO_2 and H_2O). This is higher efficiency than in the automobile engine (about 20%) and most other heat engines (maximum efficiency about 35%).

3. Formation of stalactites and stalagmites involves the dissolution and reprecipitation of calcium carbonate. Dissolved CO_2 causes limestone ($CaCO_3$) to dissolve according to the reaction $CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$. The reverse reaction results in reprecipitation of $CaCO_3$. The concentration (moles/liter) of dissolved CO_2 in water seeping through limestone caves is one factor responsible for formation of stalactites and stalagmites.

4. One source of "fixed" nitrogen (nitrogen that can be used by plants) is the combination of nitrogen and oxygen during highly energetic conditions such as during a lightning storm. The reaction is $N_2(g) + O_2(g) \rightarrow 2\,NO(g)$. The NO is further oxidized to NO_2, which dissolves in water to form nitric and nitrous acids.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

The quantities of nitrogen "fixed" is related to the moles of nitrogen reacting with oxygen.

TO THE CONTEMPORARY WORLD

Community

Knowledgeable Individuals

A pharmacist or clinical laboratory scientist (medical technologist) could explain how the mole concept is used in medicine.

Societal

1. Commercially available materials sometimes list the percent composition, particularly with respect to important or active components in the formulation. For example, the label on cleaning agents (such as dishwasher detergent) may include the percent phosphorus (by mass).
2. The composition of soil fertilizers is generally expressed in terms of % P_2O_5 (or H_3PO_4), % N (or NH_3) and % K_2O (see module on *Industrial Inorganic Chemistry*).
3. The relationship of moles to chemical reactions opens an inexhaustible supply of applications such as combustion of gasoline in automobile engines, reaction of SO_2 (from the burning of sulfur-containing fossil fuels) with $CaCO_3$ (marble, limestone, *etc.* in statuary and building materials), as well as the production of "acid rain" from SO_2. (For additional examples see module on *Stoichiometry*.)

Extensions

1. The percent water in popcorn can be determined. *Activity 2: Analyzing the "Pop" in Popcorn* in the *Gases* module provides directions.
2. A procedure for determining the percent fat and water in hot dogs is given by Tocci (1984).
3. Students could investigate methods used for determining the elemental composition of various compounds. The use of spectra in compound identification is usually beyond the scope of first-year high school chemistry; however, an outstanding student may be interested in learning what kinds of information can be obtained from various spectral techniques (*e.g.*, how atoms are connected from infrared and nuclear magnetic resonance spectra, how atoms are grouped based on how they "fall apart" from mass spectra).

References

Module developed by Caroline L. Ayers, Philip Dail, and Carolyn Morse, the North Carolina team.

Alexander, M. D., Ewing, G. J., and Abbott, F. T. (1984). Analogies that indicate the size of atoms and molecules and the magnitude of Avogadro's number. *Journal of Chemical Education*, *61*, 591.

Corwin, C. (1988). Avogadro's number. In W. S. Seese and G. W. Daub (Eds.), *Laboratory experiments for basic chemistry* (5th Ed.)(pp. 111 - 115). Englewood Cliffs, NJ: Prentice Hall.

This is one example of a laboratory activity to estimate Avogadro's number.

Dickson, T. R. (1983). Empirical formula. In *Laboratory experiments for introduction to chemistry* (4th Ed.) (pp 47-56). New York, NY: Wiley.

This experiment is typical of those illustrating the determination of the empirical formula of MgO.

Knox, K. (1980). Empirical formulas—a ratio problem. *Journal of Chemical Education, 57,* 879.

This article describes an exercise in using the female-male composition of a class to determine an empirical formula.

Kolb, D. (1978). The mole. *Journal of Chemical Education, 55,* 728-732.

This article is a review of the mole concept. It also describes methods for measuring Avogadro's number.

Morrison, P., and Morrison, P. (1987). *The ring of truth: An inquiry into how we know what we know*. New York, NY: Random House.

This book contains pictures from the videotape "The Atom" from the *Ring of Truth* series by Philip Morrison.

Morrison, P., Morrison, P., and the Office of Charles and Ray Eames. (1982). *Powers of ten.* Redding, CT: Scientific American Library.

This book illustrates orders of magnitude from 10^{24} m (larger than our galaxy) to the size of nuclei. It contains pictures taken from the film *Powers of Ten: A Film Dealing with the Relative Size of Things in the Universe and the Effect of Adding Another Zero* produced in the office of Charles and Ray Eames for IBM in 1977.

Schwartz, A. T., and Pryde, L. T. *Mole poster*. Available from Education Division, American Chemical Society, 1155 16th Street, N.W., Washington, DC 20036.

Many mole analogies presented in this module are taken from this poster.

Slowinski, E. J., Wolsey, W. C., and Masterton, W. L. (1985). Water of hydration. In *Chemical principles in the laboratory* (4th Ed.)(pp. 37-42). New York, NY: Saunders.

This is an example of a typical water of hydration experiment.

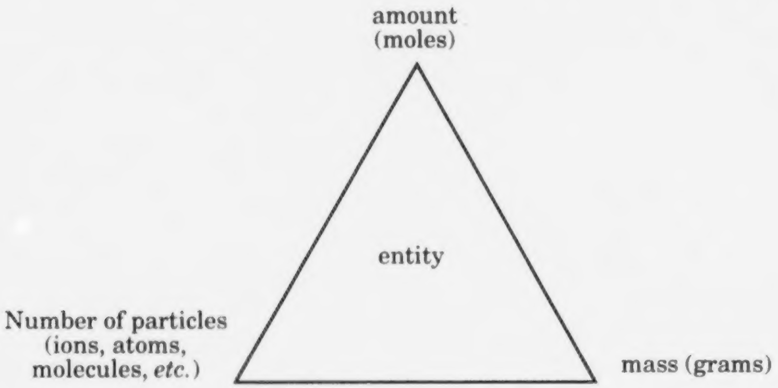
Tocci, S. (1984). How much meat in a hot dog? *The Science Teacher*, *51*(3), 62.

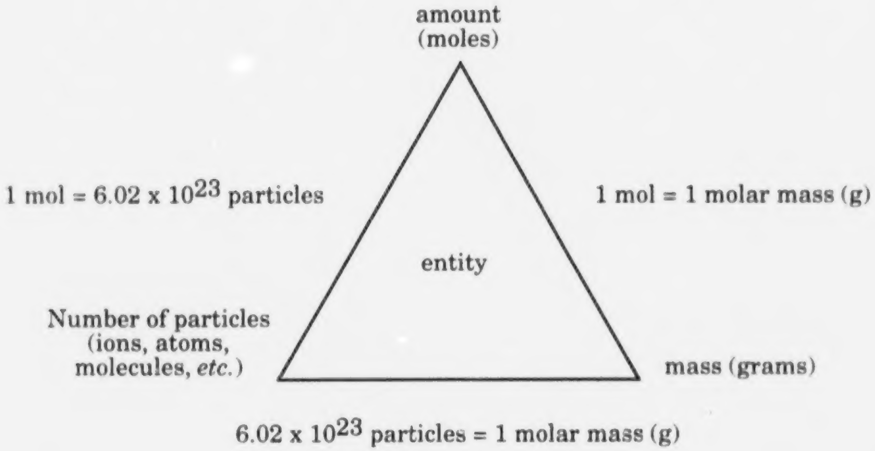
A brief description is given of a method for determining the percent fat and percent water in a hot dog.

Appendix

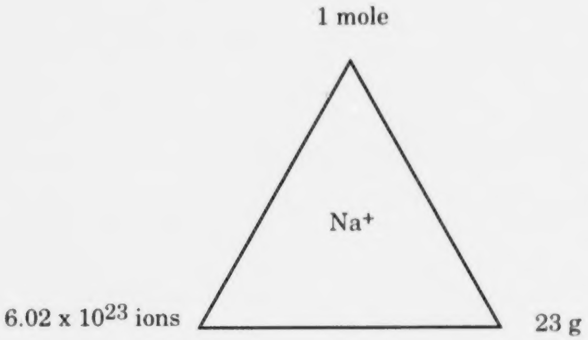
- **Transparency Masters**
  1. Triangular Relationship among Amount, Mass, and Number of Particles for an Entity
  2. Examples of Triangular Relationship
  3. Word Search
- **Humor**
  1. Mole Pattern
  2. Cartoons

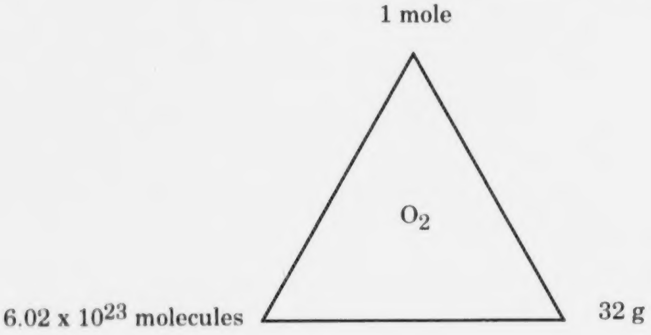
Triangular Relationship among Amount, Mass, and Number of Particles for an Entity

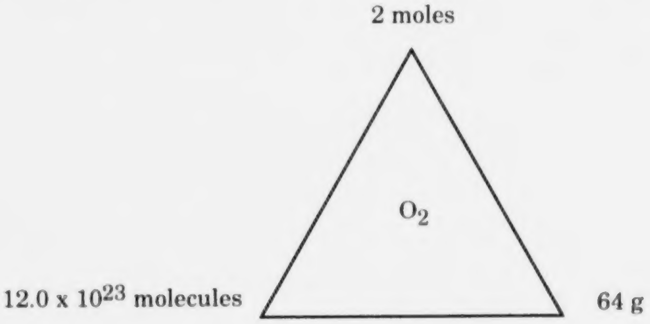




Examples of Triangular Relationship







Word Search

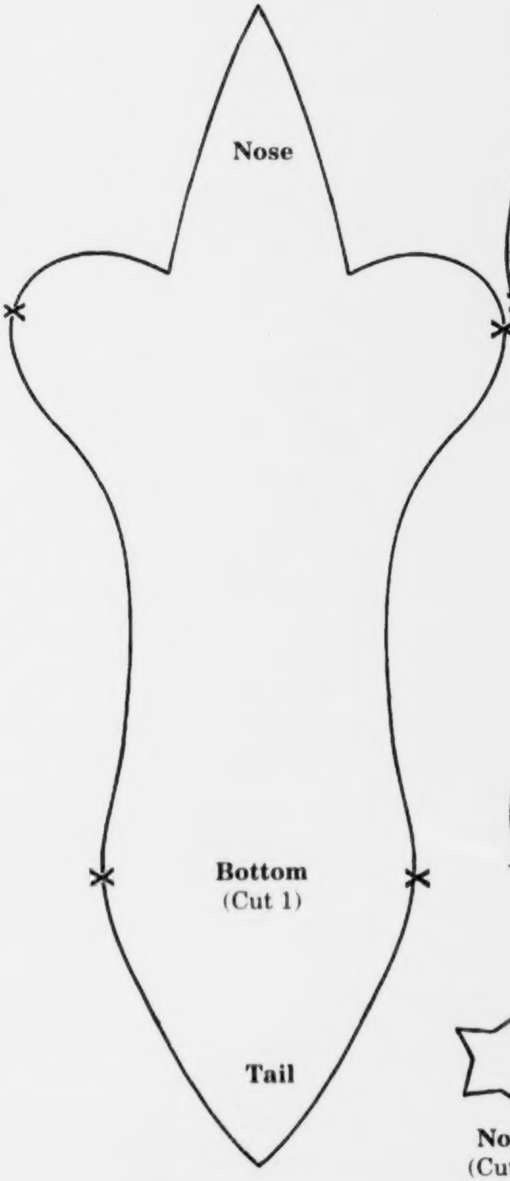
A	V	O	G	A	D	R	O	S	N	U	M	B	E	R	O	T
G	T	F	V	C	M	C	L	S	S	D	S	A	Y	K	K	S
I	V	I	O	B	D	D	X	S	M	R	L	J	J	V	X	T
A	V	I	O	W	S	Y	V	A	R	U	H	U	E	N	E	N
O	U	M	D	S	V	N	O	M	M	W	B	D	F	W	J	E
Y	G	R	A	M	O	H	W	R	J	U	T	S	A	M	B	I
S	Q	W	O	B	X	X	O	A	V	X	T	D	A	G	O	C
T	V	N	R	R	T	F	T	L	Z	B	P	F	D	G	L	I
E	D	A	Y	R	T	E	M	O	I	H	C	I	O	T	S	F
D	C	F	Z	B	G	T	I	M	S	N	W	X	Y	R	D	F
M	C	M	O	L	E	C	U	L	E	S	A	X	A	L	P	E
S	T	W	X	T	I	Z	Y	L	U	E	L	O	M	J	K	O
D	X	R	I	I	O	O	C	D	R	S	F	W	U	G	K	C

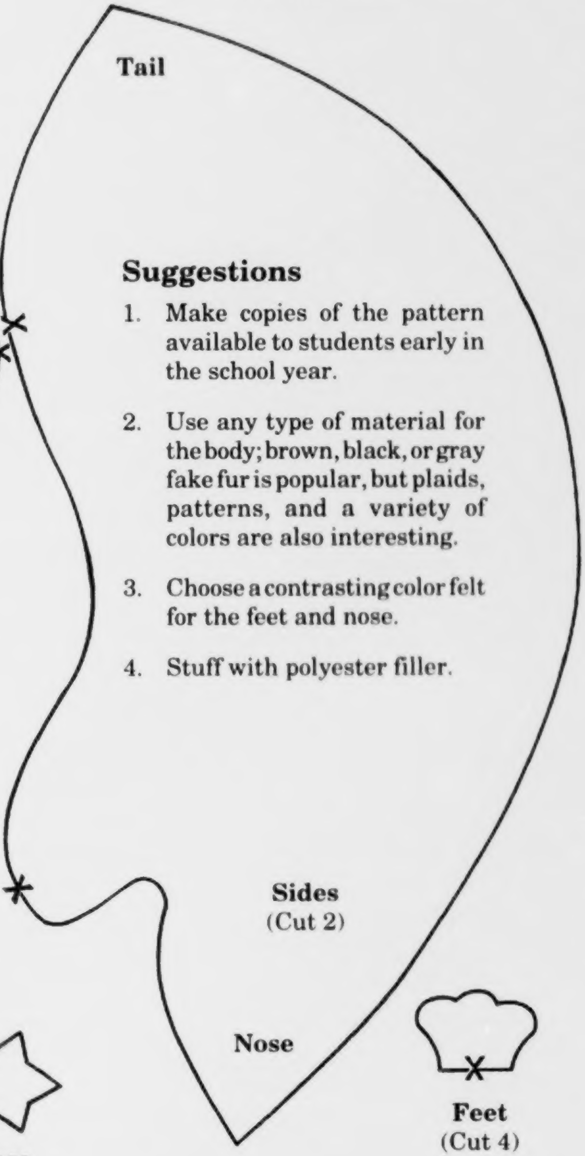
Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. A ____ of a substance represents Avogadro's number of units of that substance.
2. 6.02×10^{23} (2 words).
3. Mass, in grams, of 1 mole of a substance (2 words).
4. SI unit of mass $\div$ 1000
5. __________ describes the quantitative relationships among elements and compounds as they undergo chemical changes.
6. Symbolism showing a substance's chemical composition.
7. Smallest units of compounds.
8. Numerical multipliers showing ratios between reactants and products in a chemical equation.
9. One mole of a substance in this state at STP occupies a volume of 22.4 L.
10. One mole of this element weighs 12.0 g.

(Adapted by Ray Bruzan from a pattern obtained from Claire Smith [retired], Mills College, who discovered the original mole in an art store in Maine. Ready-made mole price list available from DeWayne Lieneman, 2509 59th St., Woodridge, IL 60517; (708) 810-0335.)

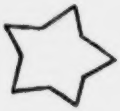
Mole Pattern

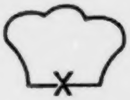


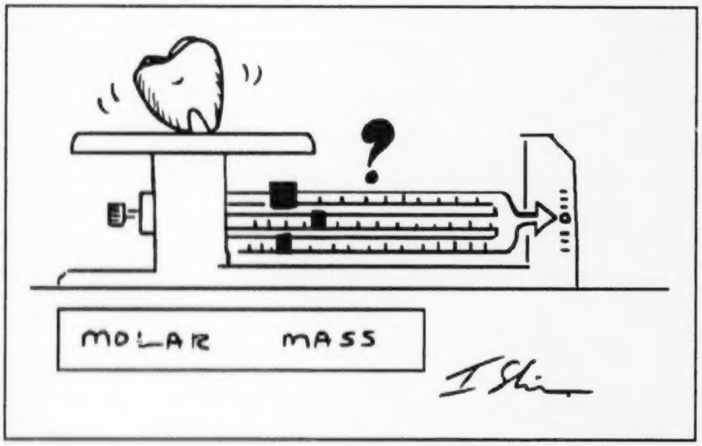


Suggestions

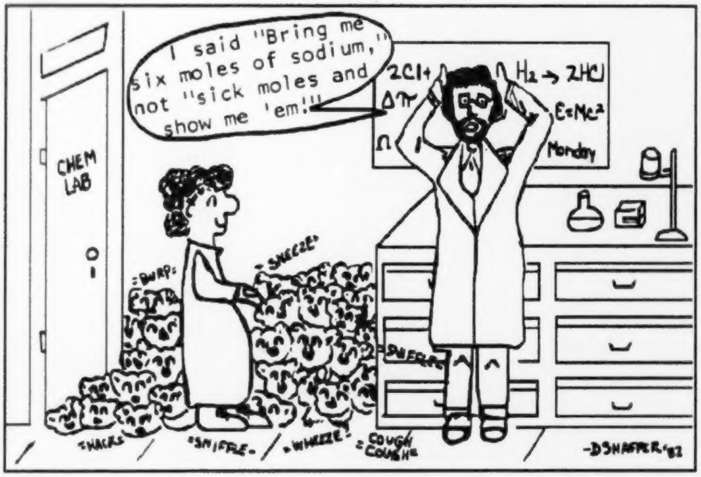
1. Make copies of the pattern available to students early in the school year.
2. Use any type of material for the body; brown, black, or gray fake fur is popular, but plaids, patterns, and a variety of colors are also interesting.
3. Choose a contrasting color felt for the feet and nose.
4. Stuff with polyester filler.







Copied with permission from CHEM 13 NEWS, January 1990, p. 12. Cartoonist: Ian Skinner, teacher at Harwood Secondary School, Ajax, ON.



CHEM 13 NEWS, May 1982, p. 14. Reprinted with permission.

OH NO, NOT MOLES AGAIN!

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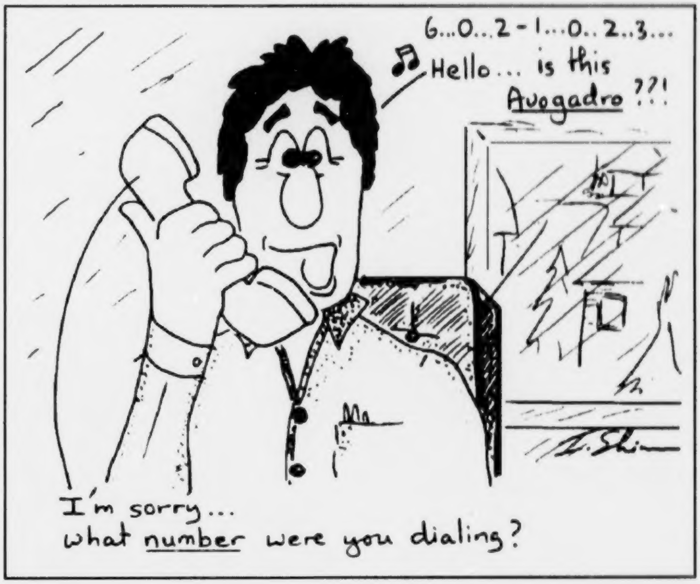
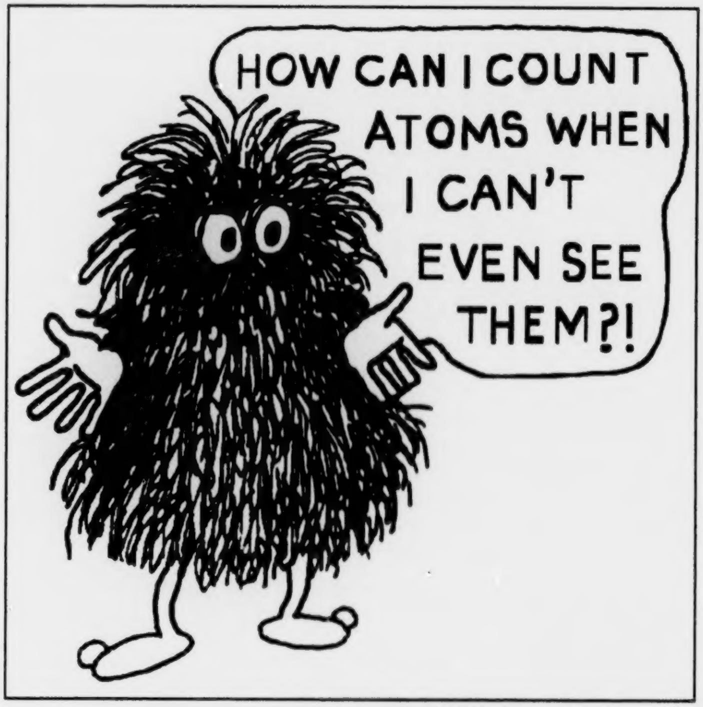

6...0...2-1...0..2..3...
Hello... is this Avogadro ??!
I'm sorry... what number were you dialing?

CHEM 13 NEWS, September & October 1987, p. 6. Reprinted with permission.


HOW CAN I COUNT ATOMS WHEN I CAN'T EVEN SEE THEM?!

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AND NOW FOR OUR NEXT NUMBER, HERE ARE AVOGADRO AND THE MOLES!
6 × 10²³

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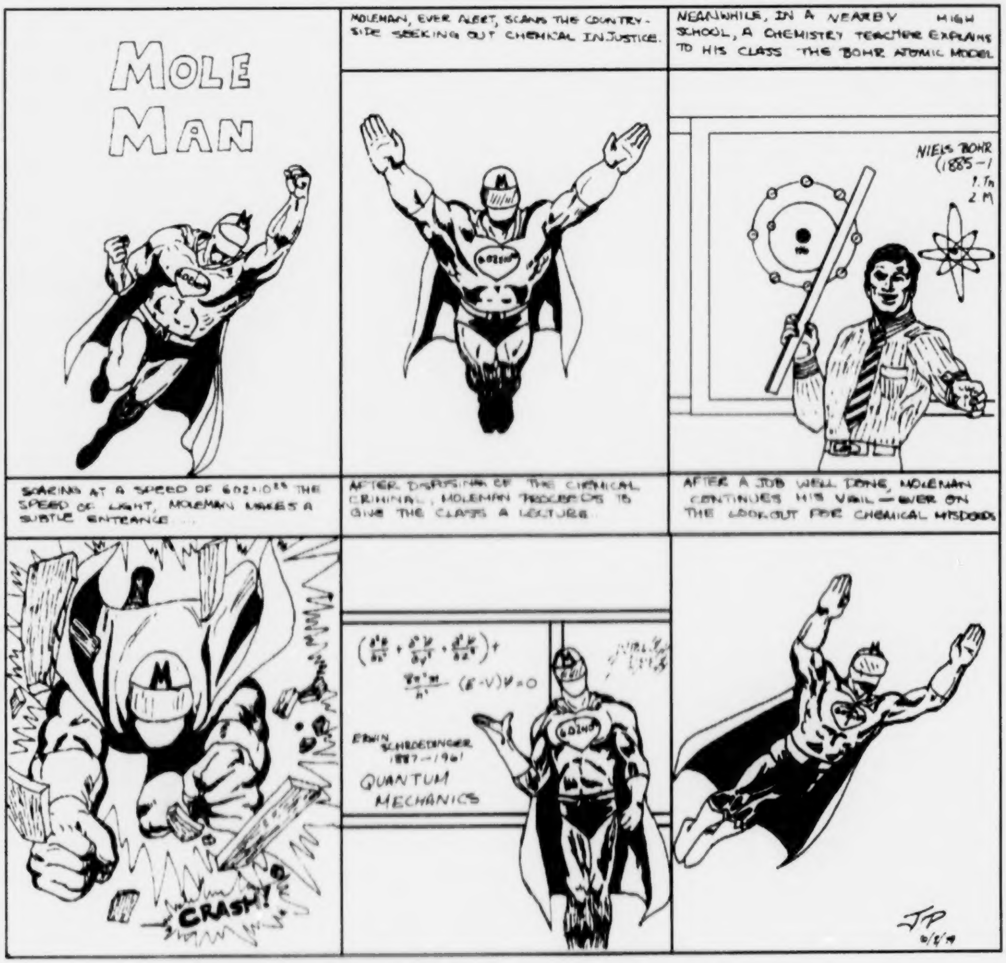
MOLE MAN
MOLEMAN, EVER ALERT, SCANS THE COUNTRYSIDE SEEKING OUT CHEMICAL INJUSTICE.
MEANWHILE, IN A NEARBY HIGH SCHOOL, A CHEMISTRY TEACHER EXPLAINS TO HIS CLASS THE BOHR ATOMIC MODEL
NIELS BOHR (1885–1
SOARING AT A SPEED OF 6.02×10²³ THE SPEED OF LIGHT, MOLEMAN MAKES A SUBTLE ENTRANCE . . .
AFTER DISPOSING OF THE CHEMICAL CRIMINAL, MOLEMAN PROCEEDS TO GIVE THE CLASS A LECTURE . . .
AFTER A JOB WELL DONE, MOLEMAN CONTINUES HIS VIGIL — EVER ON THE LOOKOUT FOR CHEMICAL MISDEEDS
CRASH!
ERWIN SCHROEDINGER 1887–1961
QUANTUM MECHANICS
JP 6/8/79

CHEM 13 NEWS, November 1979, p. 6. Reprinted with permission.

FROM THE LAB OF THE GREAT AMADEO AVOGADRO COMES THE MOST AMAZING CHEMICAL SUPERHERO OF OUR TIME, THE ONE WHO IS KNOWN AS ....
MOLE MAN
MOLE MAN, WHILE MAKING HIS DAILY ROUND, IS UNAWARE THAT ON THE OTHER SIDE OF TOWN, AN UNSPEAKABLE CRIME IS TAKING PLACE......
LORD'S RULE
$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
LET'S SWITCH THE CO-EFFICIENTS OF THAT THERE EQUATION!
MOLE MAN HEARS THE STOIC- MISDEED AND FLIES TOWA SCENE ....
MOLEMAN CORRECTS THE EQUATION, AND DEPOSITS THE THUGS IN THE PROPER RECEPTACLE
THAT SHOULD TAKE CARE OF THE THREE OF YOU!
AND SO, AS QUICKLY AS HE CAME, MOLEMAN MAKES HIS DEPARTURE. AS THE SUN SETS OVER THE CITY, PEACE IS RESTORED, AND MOLEMAN RETURNS TO AVOGADRO'S LAB. THE STREETS CAN NOW BE WALKED SAFELY BY BALANCED EQUATIONS, BUT YOU CAN BE SURE THAT WHEREVER CHEMICAL INJUSTICE IS COMMITTED, MOLE MAN WILL ONCE AGAIN APPEAR.
END
MOLEMAN™
BY JORDAN PUTTKIN, MARK TANNAUER, EZRA DOLNICK

CHEM 13 NEWS, April 1980, p. 8. Reprinted with permission.